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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

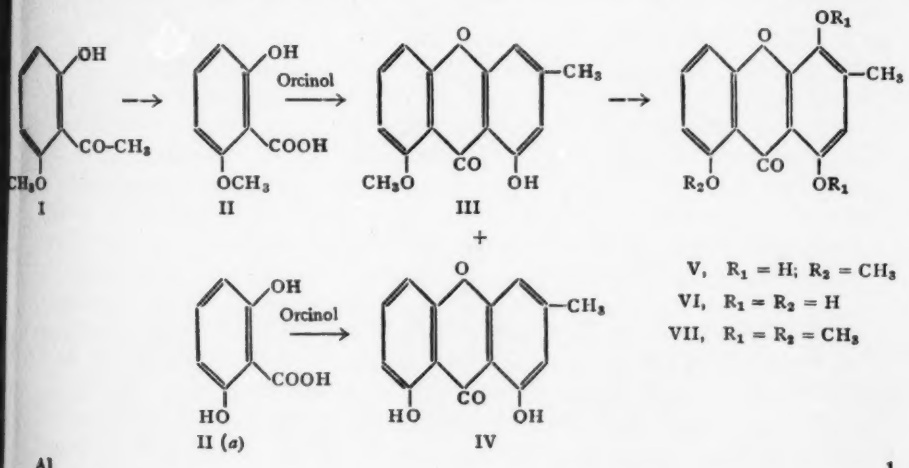
Part L. A Synthesis of Ravenelin

By V. K. Ahluwalia and T. R. Seshadri, F.A.Sc.

Received May 1, 1956

Ravenelin[1] is a yellow xanthone occurring in the mycelium of *Helminthosporum ravenelii*, and of *H. turcicum*. These moulds are rather exceptional as compared with the numerous other species of Helminthosporum which contain anthraquinone derivatives. The constitution of ravenelin was established by Raistrick *et al.*,[1] and its synthesis carried out by Mull and Nord[2] utilising Ullmann's method. Since it has a quinol structure, a synthesis involving nuclear oxidation appeared to be more convenient. The feasibility of this procedure was shown by the earlier work of Rao and Seshadri[3] who prepared 4-hydroxy euxanthone and that of Pankajamani and Seshadri[4] who made 1 : 4-dihydroxy xanthone. The method now finally adopted for the synthesis of ravenelin involves the Nencki reaction and nuclear oxidation with alkaline persulphate. The details are given below:

2-Hydroxy-6-methoxy benzoic acid (II) obtained by the oxidation of the corresponding acetophenone (I) was condensed with orcinol in presence of zinc chloride. The product is found to be a mixture which could be separated by employing their difference in solubility in ethyl alcohol.

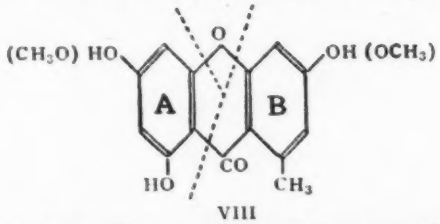


The more soluble fraction was 1-hydroxy-8-methoxy-3-methyl xanthone (III) and the less soluble one consisted of 1 : 8-dihydroxy-3-methyl xanthone (IV). The latter (IV) can also be readily obtained by the direct condensation of γ-resorcylic acid (II *a*) with orcinol. In these reactions orcinol is active in the γ-position as the resulting xanthones give sparingly soluble alkali salts and are insoluble in aqueous sodium carbonate. This γ-reactivity of orcinol was reported earlier by Shah and co-workers[5] using their modified Nencki reaction. The same xanthones have been obtained also by the modified Nencki reaction using zinc chloride and phosphorus oxychloride but the yields are comparatively high. The demethylation of the 8-position seems to proceed even more easily in this condensation though it is done at a lower temperature.

Oxidation of 1-hydroxy-8-methoxy-3-methyl xanthone (III) with alkaline persulphate gives the 1 : 4-dihydroxy compound (V), which when subjected to demethylation with hydriodic acid yields ravenelin (VI) and on methylation gives ravenelin methyl ether (VII).

The observation that ravenelin is soluble in aqueous sodium bicarbonate would appear to be rather extraordinary. The 1 : 8-dihydroxy xanthone (IV) does not dissolve even in sodium carbonate. Hydroxyl groups in the positions para to the carbonyl, *i.e.*, 3 and 6 positions in xanthones are usually considered to be acidic, but in the present case a different hydroxyl in the 4-position has enhanced this property so much that the substance becomes soluble in aqueous sodium bicarbonate.

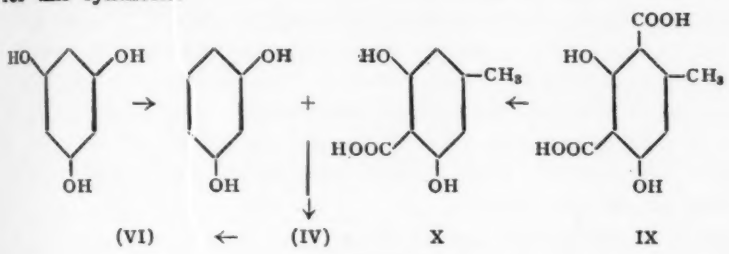
The structure of ravenelin (VI) could be considered to be derived essentially from two parts: (1) orcinol and (2) phloroglucinol linked together by a single carbon atom. The former has undergone oxidation into a hydroxy orcinol unit and the latter reduction into a resorcinol unit.



VIII

It has been stated that *H. ravenelii* and *H. turcicum* differ from the majority of H. species in producing a xanthone instead of anthraquinone as a metabolic product. However, there is partial resemblance also. As explained in an earlier publication by Aghoramurty and Seshadri,[6] anthraquinones consist of the combination of two C_8 units; in the xanthone,

ravenelin, there is one C_8 unit. It may further be mentioned that ravenelin is an isomer of lichexanthone which is the only xanthone occurring in lichens. Lichexanthone is also built up of a phloroglucinol and of an orcinol unit; but in it the β-position of the orcinol unit is involved in the condensation. Probably the correct way of analysing the lichexanthone skeleton would be as shown in the formula (VIII), a C_8-orsellinic acid unit (A) condensing with phloroglucinol (B). From the same standpoint ravenelin could be derived from an orsellinic acid unit and phloroglucinol involving more steps. 3-Carboxy orsellinic acid[7] (IX) would be the first stage undergoing decarboxylation to *p*-orsellinic acid (X), and condensation with resorcinol followed by nuclear oxidation may be the final stages. This would suggest that the lichen xanthone and mould xanthone have a number of stages common and would support the contention that the fungal part of the lichen is responsible for this synthesis.



Experimental

Condensation of 2-*hydroxy*-6-*methoxy benzoic acid and orcinol*: 1-*Hydroxy*-8-*methoxy*-3-*methyl xanthone* (*III*) *and* 1 : 8-*Dihydroxy*-3-*methyl xanthone* (*IV*)

A mixture of 2-hydroxy-6-methoxy benzoic acid (1 g.) and freshly fused zinc chloride (2 g.) was heated to 160° and kept at that temperature for 5 min. to bring it into a uniform melt. Then the temperature was brought down to 140° and maintained for 4 hrs. The product was treated with hot water (50 c.c.), cooled and extracted with ether. The ether solution was washed with dilute sodium carbonate (5%) and left in contact with sodium hydroxide solution (10%, 50 c.c.) with occasional shaking. The precipitated sodium salt was filtered off, suspended in water containing a few drops of concentrated hydrochloric acid and boiled for 10 minutes. The mixture of mono- and di-hydroxy xanthones separated out as a colourless mass and was crystallised from ethyl alcohol. The more soluble fraction (50 mg.) was 3-methyl-1-hydroxy-8-methoxy xanthone (III). It was finally crystallised from methyl alcohol yielding colourless fibrous hairy needles. It melted

at 140–41° (Found: C, 70·3; H, 4·7; $C_{15}H_{12}O_4$ requires C, 69·8; H, 4·6%). With alcoholic ferric chloride it gave a green colour. The acetate prepared with acetic anhydride and pyridine melted at 155–56°. The less soluble product (50 mg.) was 1:8-dihydroxy-3-methyl xanthone (IV). After two crystallisations from ethyl alcohol it separated as colourless thin rhombic plates and melted at 193–94° (Found: C, 69·7; H, 4·5; $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·2%). It gave a green colour with alcoholic ferric chloride. The acetate prepared by the usual method melted at 196–97°. The same products were obtained by carrying out the condensation at a lower temperature (60–70°) and employing a mixture of zinc chloride and phosphorus oxychloride as condensing agent. The yields of the monohydroxy and dihydroxy compounds were 100 mg. and 400 mg. respectively from 1 g. of of the acid.

A sample of 1:8-dihydroxy-3-methyl xanthone (IV) was prepared also by condensing 2:6-dihydroxy benzoic acid (1 g.), orcinol (1 g.) and zinc chloride (3 g.) as given above. It was isolated as the sodium salt and finally crystallised from ethyl alcohol, m.p. 193–94°. Yield 100 mg. Mixed m.p. with the product obtained above was undepressed. The same product (mixed m.p. undepressed) was obtained by carrying out the reaction at a lower temperature (60–70°) in presence of phosphorus oxychloride. Yield 400 mg. from 1 g. of the acid.

1:4-*Dihydroxy*-8-*methoxy*-3-*methyl xanthone* (*V*)

A stirred solution of 1-hydroxy-8-methoxy-3-methyl xanthone (1 g.) in pyridine (30 c.c.) and aqueous sodium hydroxide (1·5 g. in 25 c.c. water), at 15–20°, was treated dropwise with potassium persulphate (2 g.) in water (75 c.c.) during 2 hrs. After 24 hrs. at room temperature the deep brown solution was acidified to congo red and the unchanged product filtered off, ether extraction removing the last traces of it. The clear brown aqueous solution was heated in a boiling water-bath with sodium sulphite (4 g.) and concentrated hydrochloric acid (50 c.c.) for 1 hr. It was then cooled and the yellow solid was filtered off and washed with water. The filtrate on ether extraction gave some more of the quinol. It crystallised from ethyl acetate-petroleum ether mixture as orange yellow rectangular plates and melted at 250–52° (decomp.) (Found: C, 66·1; H, 4·3; $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%). It gave a brown colour with alcoholic ferric chloride and was sparingly soluble in sodium bicarbonate solution. The diacetate prepared by the acetic anhydride-pyridine method melted at 175–76°.

On methylation with methyl sulphate in acetone and potassium carbonate it gave the methyl ether (1:4:8-trimethoxy-3-methyl xanthone), which

on crystallisation from methyl alcohol melted at 179–80°, agreeing with that recorded for methyl ravenelin.[1]

1:4:8-*Trihydroxy-3-methyl xanthone* (*VI*) (*Ravenelin*)

1:4-Dihydroxy-8-methoxy-3-methyl xanthone (0·2 g.) was dissolved in acetic anhydride (5 c.c.) and to the cold solution was added hydriodic acid (5 c.c.). The solution was refluxed for two hours in an oil-bath at 145–50°. It was then poured into ice-cold saturated solution of sodium bisulphite (50 c.c.). The solid product was filtered, dried and crystallised from benzene yielding yellow needles and rectangular rods, m.p. 268–70°. Yield 0·1 g. Mixed m.p. with the natural sample of ravenelin was undepressed. Both the samples had the same absorption spectrum in the visible region with a marked maximum at 400 mμ. The acetate prepared by the acetic anhydride-pyridine method melted at 204–05° agreeing with the earlier record.

We are grateful to Prof. Raistrick, F.R.S., for kindly supplying us with a natural sample of ravenelin.

Summary

2-Hydroxy-6-methoxy benzoic acid condenses with orcinol giving rise to (1) 1-hydroxy-3-methyl-8-methoxy xanthone and (2) 1:8-dihydroxy-3-methyl xanthone. The second is also obtained from γ-resorcylic acid. The first undergoes nuclear oxidation with alkaline persulphate to yield ravenelin-8-methyl ether which is demethylated to ravenelin.

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HARMONIC ANALYSIS OF THE SPATIAL FLOW OF AN INCOMPRESSIBLE VISCOUS FLUID*

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THE laminar motion of a viscous fluid is governed by the dynamical equations of Navier-Stokes and the equation of continuity expressing a kinematical condition, *viz.*, conservation of mass. The equations of motion are of the second order and contain non-linear terms and the discussion of the equations in a general manner cannot be expected. In any particular problem the exact equations of motion are replaced by approximate ones that arise after making some simplifying assumptions and the validity of any working hypotheses that are made in the solution needs to be examined. The exact equations do not also lend themselves to the application of the methods of integral transforms in general, due to the presence of non-linear terms. A procedure was however shown by J. Kampé de Fériet[1] for setting up relations between the Fourier transforms of the various physical quantities that enter into the problem in the case of viscous liquids. He considers the plane flow of viscous liquids and expresses the transforms of the stream function and the velocity components in terms of the transform of the vorticity and shows that the vorticity transform satisfies an integro-differential equation.

In the present paper we are concerned with the harmonic analysis of the spatial flow of an incompressible viscous fluid *first* in a bounded domain D with a regular boundary surface Γ when the velocity components u, v, $w = 0$ on Γ and *second* when the flow region is the entire space in which case the velocity components are assumed to vanish sufficiently strongly at infinity. We set up relations between the triple Fourier transforms of the velocity and vorticity components and obtain bounds for the spectral function of the kinetic energy of the flow (Theorems I and II below). It is true that the technique of the Fourier transform is best employed with respect to the time variable for the concerned equations are invariant with respect to a translation in time. However the boundary conditions satisfied

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by the velocity components in the first case or their behaviour at infinity in the second case enable us to employ successfully the Fourier transform with respect to the space variables. We show that the transforms of the vorticity components are governed by three non-linear integro-differential equations (Theorem IV below) which may be considered an extension to three dimensions of Theorem IV in Kampé de Fériet's paper.[1] These equations are completely integrated in a special case and a method of building up solution is described when the non-linear terms do not have an appreciable effect.

In the case of viscous flow in a bounded domain D with a regular boundary Γ, the flow velocity $\vec{q} = (u, v, w) = 0$ on Γ. The Fourier transforms of the velocity components are

$$\mathrm{U}(\omega_1, \omega_2, \omega_3, t) = \frac{1}{8\pi^3} \int\int_{\mathrm{D}}\int u(x, y, z, t) \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dxdydz,$$

$$\mathrm{V}(\omega_1, \omega_2, \omega_3, t) = \frac{1}{8\pi^3} \int\int_{\mathrm{D}}\int v(x, y, z, t) \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dxdydz,$$

$$\mathrm{W}(\omega_1, \omega_2, \omega_3, t) = \frac{1}{8\pi^3} \int\int_{\mathrm{D}}\int w(x, y, z, t) \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dxdydz.$$

If $\vec{\zeta} = \operatorname{curl} \vec{q} = (\xi, \eta, \zeta)$ is the vorticity vector and $\mathrm{X}(\omega_1, \omega_2, \omega_3, t)$, $\mathrm{Y}(\omega_1, \omega_2, \omega_3, t)$, $\mathrm{Z}(\omega_1, \omega_2, \omega_3, t)$ are the Fourier transforms of ξ, η, ζ we may easily derive the relations

$$\mathrm{X} = i(\omega_3 \mathrm{V} - \omega_2 \mathrm{W}),\ \mathrm{Y} = i(\omega_1 \mathrm{W} - \omega_3 \mathrm{U}),\ \mathrm{Z} = i(\omega_2 \mathrm{U} - \omega_1 \mathrm{V}) \qquad (1)$$

so that we have

$$|\mathrm{X}| \leqslant |\omega_3 \mathrm{V}| + |\omega_2 \mathrm{W}|,\ |\mathrm{Y}| \leqslant |\omega_1 \mathrm{W}| + |\omega_3 \mathrm{U}|,\ |\mathrm{Z}| \leqslant |\omega_2 \mathrm{U}| + |\omega_1 \mathrm{V}| \qquad (2)$$

and

$$\omega_1 \mathrm{X} + \omega_2 \mathrm{Y} + \omega_3 \mathrm{Z} = 0.$$

We may note here also that

$$\omega_1 \mathrm{U} + \omega_2 \mathrm{V} + \omega_3 \mathrm{W} = 0. \qquad (3)$$

From (1) and (3) we may express the transforms of the velocity components in terms of those of the vorticity components, which we state as

THEOREM I.—The velocity transforms are related to the vorticity transforms by means of the equations

$$U = \frac{i[\omega_3 Y - \omega_2 Z]}{\omega_1^2 + \omega_2^2 + \omega_3^2}, \quad V = \frac{i[\omega_1 Z - \omega_3 X]}{\omega_1^2 + \omega_2^2 + \omega_3^2},$$

$$W = \frac{i[\omega_2 X - \omega_1 Y]}{\omega_1^2 + \omega_2^2 + \omega_3^2}. \tag{4}$$

The kinetic energy of the flow is

$$T = \frac{\rho}{2} \int\int_D\int q^2 dxdydz = \frac{\rho}{2} \int\int_D\int (u^2 + v^2 + w^2)\, dxdydz$$

$$= 4\pi^3\rho \int\int_\Omega\int (U\bar{U} + V\bar{V} + W\bar{W})\, d\omega_1 d\omega_2 d\omega_3$$

by Parseval's theorem. Ω is the infinite domain $-\infty < \omega_1, \omega_2, \omega_3 < \infty$ in the space of real variables $\omega_1, \omega_2, \omega_3$. If $\gamma(\omega_1, \omega_2, \omega_3, t)$ is the spectral function of the kinetic energy, then we have

$$T = \int\int_\Omega\int \gamma(\omega_1, \omega_2, \omega_3, t)\, d\omega_1 d\omega_2 d\omega_3.$$

Comparing this with the relation immediately above, and using Theorem I we have

THEOREM II.—The spectral function $\gamma(\omega_1, \omega_2, \omega_3, t)$ of the kinetic energy T is expressed in terms of the Fourier transforms of the velocity or vorticity components in the form

$$\gamma(\omega_1, \omega_2, \omega_3, t) = 4\pi^3\rho(|U|^2 + |V|^2 + |W|^2)$$

$$= 4\pi^3\rho(|X|^2 + |Y|^2 + |Z|^2)/(\omega_1^2 + \omega_2^2 + \omega_3^2). \tag{5}$$

Now, by Schwarz's inequality we have relations of the form

$$|U(\omega_1, \omega_2, \omega_3, t)|^2 \leqslant \frac{\text{Vol. (D)}}{64\pi^6} \int\int_D\int u^2 dxdydz$$

so that

$$\gamma(\omega_1, \omega_2, \omega_3, t) \leqslant 4\pi^3\rho \frac{\text{Vol. (D)}}{64\pi^6} \int\int_D\int (u^2 + v^2 + w^2)\, dxdydz$$

$$= \frac{\text{Vol. (D)}}{8\pi^3} T.$$

Inequalities can be obtained also for the transforms of the velocity and vorticity components. We may note that each of $|U|, |V|, |W|$ satisfies the inequality

$$(|U| \text{ or } |V| \text{ or } |W|) \leqslant B(T)^{\frac{1}{2}}$$

where

$$B = \frac{1}{8\pi^3}\left(\frac{2}{\rho}\,\text{Vol.}(D)\right)^{\frac{1}{2}}$$

and

$$|X| \leqslant B(|\omega_2| + |\omega_3|)(T)^{\frac{1}{2}},\quad |Y| \leqslant B(|\omega_3| + |\omega_1|)(T)^{\frac{1}{2}},$$
$$|Z| \leqslant B(|\omega_1| + |\omega_2|)(T)^{\frac{1}{2}}.$$

The kinetic energy of the flow can also be expressed in the form

$$T = \frac{\rho}{8\pi}\int\int\int_D \int\int\int_D \frac{(\text{curl}\,\vec{q})_P \cdot (\text{curl}\,\vec{q})_Q}{PQ}\,(dxdydz)_P\,(dxdydz)_Q \qquad (6)$$

from which we have

$$T \leqslant \frac{\rho A}{8\pi}\int\int\int_D (\text{curl}\,\vec{q})^2\,dxdydz$$

and

$$T \leqslant T_0 \exp\left(-\frac{8\pi\nu}{A}\,t\right). \qquad (7)$$

The quantity A in these expressions is a positive constant depending only on the domain D and is given by

$$A^2 = \int\int\int_D \int\int\int_D \frac{(dxdydz)_P\,(dxdydz)_Q}{PQ^2} \qquad (8)$$

Using (7) in the above inequalities for the transforms of the vorticity components we have

THEOREM III.—The upper bounds for the vorticity transforms and the spectral functions are always decreasing with respect to time and

$$|X| \leqslant B(|\omega_2| + |\omega_3|)(T_0)^{\frac{1}{2}} \exp\left(-\frac{4\pi\nu}{A}\,t\right),$$

$$|Y| \leqslant B(|\omega_3| + |\omega_1|)(T_0)^{\frac{1}{2}} \exp\left(-\frac{4\pi\nu}{A}\,t\right),$$

$$|Z| \leqslant B(|\omega_1| + |\omega_2|)(T_0)^{\frac{1}{2}} \exp\left(-\frac{4\pi\nu}{A}\,t\right),$$

$$\gamma(\omega_1, \omega_2, \omega_3, t) \leqslant \frac{\text{Vol. (D)}}{8\pi^3} \, T_0 \exp\left(-\frac{8\pi\nu}{A} t\right). \tag{9}$$

The harmonic analysis of the flow of an incompressible fluid can be based on the study of the Fourier transform functions $X(\omega_1, \omega_2, \omega_3, t)$, $Y(\omega_1, \omega_2, \omega_3, t)$, $Z(\omega_1, \omega_2, \omega_3, t)$ of the vorticity vector (ξ, η, ζ). The form of these functions cannot be determined in a general case and we derive below three non-linear integro-differential equations, the solutions of which determine X, Y, Z.

The equation of fluid motion can be written in the form

$$\frac{d\vec{q}}{dt} = -\operatorname{grad}\left(\Omega + \frac{p}{\rho}\right) + \nu\Delta\vec{q}, \tag{10}$$

where the notations are classical. In the case of incompressible fluids the continuity equation has the form $\operatorname{div}\vec{q} = 0$. Taking the curl on both sides of (10) and writing $\vec{\zeta} = \operatorname{curl}\vec{q}$, we have

$$\frac{d\vec{\zeta}}{dt} = (\vec{\zeta} \cdot \operatorname{grad})\vec{q} + \nu\Delta\vec{\zeta},$$

which can be written in the following scalar form.

$$\begin{aligned}
&\frac{\partial\xi}{\partial t} + u\frac{\partial\xi}{\partial x} + v\frac{\partial\xi}{\partial y} + w\frac{\partial\xi}{\partial z} = \xi\frac{\partial u}{\partial x} + \eta\frac{\partial u}{\partial y} + \zeta\frac{\partial u}{\partial z} + \nu\Delta\xi,\\
&\frac{\partial\eta}{\partial t} + u\frac{\partial\eta}{\partial x} + v\frac{\partial\eta}{\partial y} + w\frac{\partial\eta}{\partial z} = \xi\frac{\partial v}{\partial x} + \eta\frac{\partial v}{\partial y} + \zeta\frac{\partial v}{\partial z} + \nu\Delta\eta,\\
&\frac{\partial\zeta}{\partial t} + u\frac{\partial\zeta}{\partial x} + v\frac{\partial\zeta}{\partial y} + w\frac{\partial\zeta}{\partial z} = \xi\frac{\partial w}{\partial x} + \eta\frac{\partial w}{\partial y} + \zeta\frac{\partial w}{\partial z} + \nu\Delta\zeta.
\end{aligned} \tag{11}$$

Using relations of the type

$$\begin{aligned}
&\left(u\frac{\partial\xi}{\partial x} + v\frac{\partial\xi}{\partial y} + w\frac{\partial\xi}{\partial z} - \xi\frac{\partial u}{\partial x} - \eta\frac{\partial u}{\partial y} - \zeta\frac{\partial u}{\partial z}\right)\exp\left[i(\omega_1 x + \omega_2 y + \omega_3 z)\right]\\
&\quad = \frac{\partial}{\partial z}\{(w\xi - u\zeta)\exp\left[i(\omega_1 x + \omega_2 y + \omega_3 z)\right]\}\\
&\qquad - \frac{\partial}{\partial y}\{(u\eta - v\xi)\exp\left[i(\omega_1 x + \omega_2 y + \omega_3 z)\right]\}\\
&\qquad + i\{\omega_2(u\eta - v\xi) - \omega_3(w\xi - u\zeta)\}\exp\left[i(\omega_1 x + \omega_2 y + \omega_3 z)\right]
\end{aligned}$$

and taking the transforms of the above equations, we are led to integro-differential equations of the form

$$\frac{\partial \mathrm{X}(\omega_1, \omega_2, \omega_3, t)}{\partial t} + i \iiint_{\Theta} [\omega_2 \{\mathrm{U}(\theta_1, \theta_2, \theta_3, t)\, \bar{\mathrm{Y}}(\theta_1 - \omega_1, \theta_2 - \omega_2, \theta_3 - \omega_3, t) - \mathrm{V}(\theta_1, \theta_2, \theta_3, t) \cdot \bar{\mathrm{X}}(\theta_1 - \omega_1, \theta_2 - \omega_2, \theta_3 - \omega_3, t)\} - \omega_3 \{\mathrm{W}(\theta_1, \theta_2, \theta_3, t)\, \bar{\mathrm{X}}(\theta_1 - \omega_1, \theta_2 - \omega_2, \theta_3 - \omega_3, t) - \mathrm{U}(\theta_1, \theta_2, \theta_3, t)\, \bar{\mathrm{Z}}(\theta_1 - \omega_1, \theta_2 - \omega_2, \theta_3 - \omega_3, t)\}] \cdot d\theta_1\, d\theta_2\, d\theta_3 = \frac{\nu}{8\pi^3} \iiint_{\mathrm{D}} (\Delta\xi) \exp[i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dx dy dz \qquad (12)$$

where Θ is the entire space of the real variables $\theta_1, \theta_2, \theta_3$. The integrand on the left side can be written in terms of the transforms of the vorticity components. Writing $\mathrm{U}(\theta_1, \theta_2, \theta_3, t)$ as $\mathrm{U}(\theta)$ and $\mathrm{X}(\theta_1 - \omega_1, \theta_2 - \omega_2, \theta_3 - \omega_3, t)$ as $\mathrm{X}(\theta - \omega)$ (we continue this practice throughout the rest of this paper) we have

$$\mathrm{U}(\theta)[\omega_2 \bar{\mathrm{Y}}(\theta-\omega) + \omega_3 \bar{\mathrm{Z}}(\theta-\omega)] - [\omega_2 \mathrm{V}(\theta) + \omega_3 \mathrm{W}(\theta)]\, \bar{\mathrm{X}}(\theta-\omega) = \frac{i}{\theta_1^2+\theta_2^2+\theta_3^2} \{(\omega_2\theta_3 - \omega_3\theta_2)[\mathrm{X}(\theta)\, \bar{\mathrm{X}}(\theta-\omega) + \mathrm{Y}(\theta)\, \bar{\mathrm{Y}}(\theta - \omega) + \mathrm{Z}(\theta)\, \bar{\mathrm{Z}}(\theta - \omega)] - [\omega_2 \mathrm{Z}(\theta) - \omega_3 \mathrm{Y}(\theta)][\theta_1 \bar{\mathrm{X}}(\theta - \omega) + \theta_2 \bar{\mathrm{Y}}(\theta - \omega) + \theta_3 \bar{\mathrm{Z}}(\theta - \omega)]\}$$

so that (12) assumes the form

$$\frac{\partial \mathrm{X}}{\partial t} - \iiint_{\Theta} \{(\omega_2\theta_3 - \omega_3\theta_2)[\mathrm{X}(\theta)\, \bar{\mathrm{X}}(\theta - \omega) + \mathrm{Y}(\theta)\, \bar{\mathrm{Y}}(\theta - \omega) + \mathrm{Z}(\theta)\, \bar{\mathrm{Z}}(\theta-\omega)] - [\omega_2 \mathrm{Z}(\theta) - \omega_3 \mathrm{Y}(\theta)][\theta_1 \bar{\mathrm{X}}(\theta - \omega) + \theta_2 \bar{\mathrm{Y}}(\theta - \omega) + \theta_3 \bar{\mathrm{Z}}(\theta - \omega)]\}(\theta_1^2 + \theta_2^2 + \theta_3^2)^{-1} \cdot d\theta_1 d\theta_2 d\theta_3$$

$$= \frac{\nu}{8\pi^3} \iiint_D (\Delta\xi) \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dxdydz.$$

Using Green's formula we can write

$$\frac{\nu}{8\pi^3} \iiint_D (\Delta\xi) \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dxdydz$$
$$= -\nu(\omega_1^2 + \omega_2^2 + \omega_3^2)\, X(\omega_1, \omega_2, \omega_3, t)$$
$$+ \frac{\nu}{8\pi^3} \iint_\Gamma \left[\frac{\partial\xi}{\partial n} - i(l\omega_1 + m\omega_2 + n\omega_3)\xi\right] \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dS.$$

Setting

$$F(\omega_1, \omega_2, \omega_3, t) = \frac{1}{8\pi^3} \iint_\Gamma \left[\frac{\partial\xi}{\partial n} - i(l\omega_1 + m\omega_2 + n\omega_3)\,\xi\right] \times \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)] \cdot dS \quad (13)$$

and similarly $G(\omega_1, \omega_2, \omega_3, t)$, $H(\omega_1, \omega_2, \omega_3, t)$ we have

THEOREM IV.—The vorticity transform vector (X, Y, Z) is governed by the following integro-differential equation

$$\frac{\partial}{\partial t}[X, Y, Z] - \iiint_\Theta \{[\vec{\omega} X \vec{\theta}]\, [X(\theta)\, \bar{X}(\theta - \omega) + Y(\theta)\, \bar{Y}(\theta - \omega) + Z(\theta)\, \bar{Z}(\theta - \omega)] - ([\vec{\omega}] \times [X(\theta), Y(\theta), Z(\theta)]) \times [\theta_1 \bar{X}(\theta - \omega) + \theta_2 \bar{Y}(\theta - \omega) + \theta_3 \bar{Z}(\theta - \omega)]\} \cdot (\theta_1^2 + \theta_2^2 + \theta_3^2)^{-1}\, d\theta_1 d\theta_2 d\theta_3$$
$$= -\nu(\omega_1^2 + \omega_2^2 + \omega_3^2)\,[X, Y, Z] - \nu\,[F, G, H] \quad (14)$$

where $\vec{\omega} = (\omega_1, \omega_2, \omega_3)$ and $\vec{\theta} = (\theta_1, \theta_2, \theta_3)$. There is no simple method of dealing further with these equations. In the rather special case where the fluid fills the entire space and the non-linear terms are small and represent a perturbation of a linear flow, a method of building up the solution will be considered later in this paper.

The case of fluid extending over the entire space

The fluid extends over the whole space $-\infty < x, y, z < \infty$ and the velocity and vorticity components are assumed to be absolutely integrable over the whole space: *i.e.*, relations like $\int_{-\infty}^{\infty}\int\int |u(x, y, z, t)|\, dxdydz < \infty$

are satisfied so that the Fourier transforms of these quantities, now defined as

$$U(\omega_1, \omega_2, \omega_3, t) = \frac{1}{8\pi^3} \int\int\int_{-\infty}^{\infty} u(x, y, z, t) \exp [i(\omega_1 x + \omega_2 y + \omega_3 z)]\, dxdydz,$$

etc, exist. To set up the relations between the velocity and vorticity transform vectors, we take the transforms over the volume of the sphere (D_R) $x^2 + y^2 + z^2 = R^2$ and then let $R \to \infty$. We can show easily (*cf.* the third part of Ref. [1]) that the relations between the velocity and vorticity transforms (1) and (4) remain valid even now if

$$R^3 u,\ R^3 v,\ R^3 w,\ R^4 \frac{\partial u}{\partial x},\ R^4 \frac{\partial u}{\partial y},\ R^4 \frac{\partial u}{\partial z},\ R^4 \frac{\partial v}{\partial x},\ \ldots\ldots\ldots,\ R^4 \frac{\partial w}{\partial z}$$

remain bounded in absolute value as R increases and we may also see that the functions $F(\omega_1, \omega_2, \omega_3, t)$, $G(\omega_1, \omega_2, \omega_3, t)$, $H(\omega_1, \omega_2, \omega_3, t)$ defined in (13) tend to zero if $R^2\xi,\ R^2\eta,\ R^2\zeta,\ R^2 \frac{\partial \xi}{\partial x}, \ldots\ldots\ldots, R^2 \frac{\partial \zeta}{\partial z}$ tend uniformly to zero in all directions as $R \to \infty$.

THEOREM V.—In the case of a flow extending over the entire space, if the fluid is at rest at infinity and if the velocity and vorticity components decrease so rapidly that the kinetic energy is finite and all the velocity and vorticity components are absolutely integrable over the whole space, then the vorticity transform vector is governed by the integro-differential equation

$$\begin{aligned} \frac{\partial}{\partial t}[X, Y, Z] - \int\int\int_{\Theta} \{[\vec{\omega} \times \vec{\theta}]\, [X(\theta)\, \bar{X}(\theta - \omega) + Y(\theta)\, \bar{Y}(\theta - \omega) \\ + Z(\theta)\, \bar{Z}(\theta - \omega)] - ([\vec{\omega}] \times [X(\theta), Y(\theta), Z(\theta)]) \\ \times [\theta_1 \bar{X}(\theta - \omega) + \theta_2 \bar{Y}(\theta - \omega) + \theta_3 \bar{Z}(\theta - \omega)]\} \\ \cdot (\theta_1^2 + \theta_2^2 + \theta_3^2)^{-1}\, d\theta_1 d\theta_2 d\theta_3 \\ = -\nu(\omega_1^2 + \omega_2^2 + \omega_3^2)\, [X(\omega, t), Y(\omega, t), Z(\omega, t)]. \quad (15) \end{aligned}$$

In the case of Beltrami flows, the stream lines are coincident with the vortex-lines ($\vec{q} \times \operatorname{curl} \vec{q} = 0$) and the non-linear terms in the equations drop out. The vorticity transform vector then satisfies the differential equation

$$\begin{aligned} \frac{\partial}{\partial t}(X(\omega, t), Y(\omega, t), Z(\omega, t)] = -\nu(\omega_1^2 + \omega_2^2 + \omega_3^2) \\ \times [X, Y, Z] \quad (16) \end{aligned}$$

and we easily get the integral in the form

$$\begin{aligned} [X(\omega, t), Y(\omega, t), Z(\omega, t)] = [X_0(\omega), Y_0(\omega), Z_0(\omega)] \exp \\ \times [-\nu(\omega_1^2 + \omega_2^2 + \omega_3^2)\, t]. \quad (17) \end{aligned}$$

U, V, W and the spectral function are now easily obtained by (4) and (5). The equation $\frac{\partial}{\partial t}[X, Y, Z] = -\nu(\omega_1^2 + \omega_2^2 + \omega_3^2)[X, Y, Z]$ which is exactly satisfied in the case of Beltrami flows, arises also in the case of slow motions. In the case where the non-linear terms in (15) are small we may obtain an approximate solution by writing

$$[X, Y, Z] = [X_0, Y_0, Z_0] + X_1, Y_1, Z_1]$$

where $[X_0, Y_0, Z_0]$ is the solution of (16). Inserting these expressions in (15) and retaining only terms in X_0, Y_0, Z_0 in the integral, we have

$$\frac{\partial}{\partial t}[X_1, Y_1, Z_1] + \nu(\omega_1^2 + \omega_2^2 + \omega_3^2)[X_1, Y_1, Z_1]$$

$$= \iiint_{\Theta} \{([\vec{\omega} \times \vec{\theta}])[X_0(\theta)\bar{X}_0(\theta - \omega) + Y_0(\theta)\bar{Y}_0(\theta - \omega)$$

$$+ Z_0(\theta)\bar{Z}_0(\theta - \omega)] - ([\vec{\omega}] \times [X_0(\theta), Y_0(\theta), Z_0(\theta)])$$

$$\times [\theta_1\bar{X}_0(\theta - \omega) + \theta_2\bar{Y}_0(\theta - \omega) + \theta_3\bar{Z}_0(\theta - \omega)]\}$$

$$\times (\theta_1^2 + \theta_2^2 + \theta_3^2)^{-1} d\theta_1 d\theta_2 d\theta_3.$$

This is linear in $[X_1, Y_1, Z_1]$ and the initial condition is expressed by $X_1, Y_1, Z_1 = 0$ at $t = 0$. The problem is therefore easily dealt with. The above procedure can be iterated by retaining terms of the next highest order of smallness in the integral in (15). The solution obtained in this way represents a perturbation of the linear flow described by the equation $\frac{\partial}{\partial t}[\xi, \eta, \zeta] = \nu\Delta[\xi, \eta, \zeta]$.

The method of building up solution described above is applicable only when the non-linear term is not appreciable in effect [*cf.* Ref. (3)].

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THE ROLE OF SOLVENTS IN CHEMICAL REACTIONS

Part III.* The Reaction between Aniline and Methyl Iodide in Mixture of Solvents

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(Contribution from the Chemistry Department, Madras Christian College, Tambaram)

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(Communicated by Dr. S. V. Anantakrishnan, F.A.SC.)

In the previous part[1] it was observed that as the reaction progressed, separation of crystals in nitrobenzene solution indicated that strict homogeneous conditions did not hold, though for purpose of comparison, initial rates could be utilised. Also no rate studies were practicable in carbon tetrachloride. Since the reaction was found to be homogeneous in acetone, it was considered that a mixture of nitrobenzene with this solvent might be more suitable than pure nitrobenzene. Further, it was anticipated that addition of small amounts of acetone to carbon tetrachloride would make the reaction rate measurable besides giving information about the reaction in which later steps might not take place. It has been found that the addition of even 5% acetone to nitrobenzene led to homogeneous reaction while carbon tetrachloride gave measurable rates and a homogeneous initial reaction with the addition of only 10% of acetone.

The specific solvent effects other than dielectric constant noticed with the pure solvents are even more clearly illustrated by the solvent mixtures. Dealing with a number of solvents, von Halban[2] had attempted to correlate the reaction rate between amines and alkyl halides with solubility. His results showed definite trends in the values of the rate constants though he had used only the mean value for his comparisons. Further, the reactions were not homogeneous in all cases. In the previous part[1] it was noticed that though acetone and nitrobenzene have a dielectric constant of comparable magnitude, the rate was faster in the solvent of the lower dielectric constant. Nor did the results conform to the expectation that a solvent of high cohesion favours the formation of a more polar compound. To minimise complications arising from lack of homogeneity, solvent mixtures were tried. The trend in the rate constants with variations in the environment as well as the Arrhenius parameters are presented in Tables I and II

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* Based on thesis approved for Ph.D. Degree of Madras University.

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TABLE I

Solvent	Temp. °C.	Concentration of Aniline	Concentration of Methyl iodide	$k_2 \times 10^4$ Initial	$k_2 \times 10^4$ Mean value
5% Acetone-Nitrobenzene ..	50	0·09750	0·1082	3·360	3·756
	60	0·09701	0·1070	6·022	6·976
10% Acetone-Nitrobenzene ..	50	0·09744	0·1082	3·845	4·094
	60	0·09729	0·1093	6·525	8·182
25% Acetone-Nitrobenzene ..	50	0·09804	0·1065	4·513	5·197
	60	0·09826	0·1077	8·636	9·699
10% Acetone-Carbon tetrachloride	60	0·1000	0·1128	0·4060	0·4063

All concentrations are in moles per litre and all rate constants are calculated with the unit of time in seconds.

TABLE II

Solvent	Arrhenius Activation energy K.Cals.	Frequency Factor ($Log_{10}PZ$)	Rate const. (at 60° C.) $\times 10^5$
100% Acetone	13·230	5·59	78·93
75% Nitrobenzene	13·670	5·91	85·50
90% ,, ...	12·190	4·83	67·30
95% ,, ...	12·470	4·96	59·00
100% ,, ...	16·830	7·80	56·70
10% Acetone-Carbon tetrachloride	24·000	9·00	4·08
95% Ethyl alcohol	15·370	7·35	177·1

Rate constants in Acetone-Nitrobenzene mixtures were obtained by extrapolation of k_2-% reaction graph to 0% reaction.

(Ref. Figs. 1 and 2 also). Typical runs are collected together in the experimental part. The reaction has been studied only at two temperatures in the acetone-nitrobenzene mixtures and in the acetone carbon tetrachloride system only at the higher temperature; comparable concentrations of the reactants have been used in all the cases. In the more polar solvent mixture,

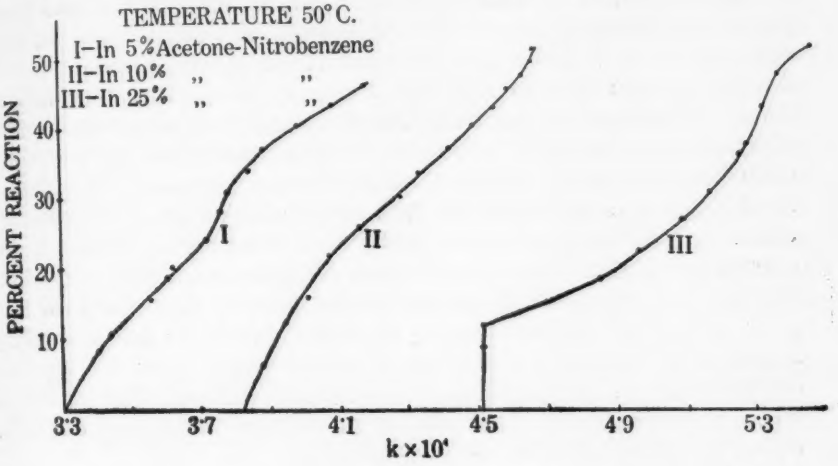

FIG. 1

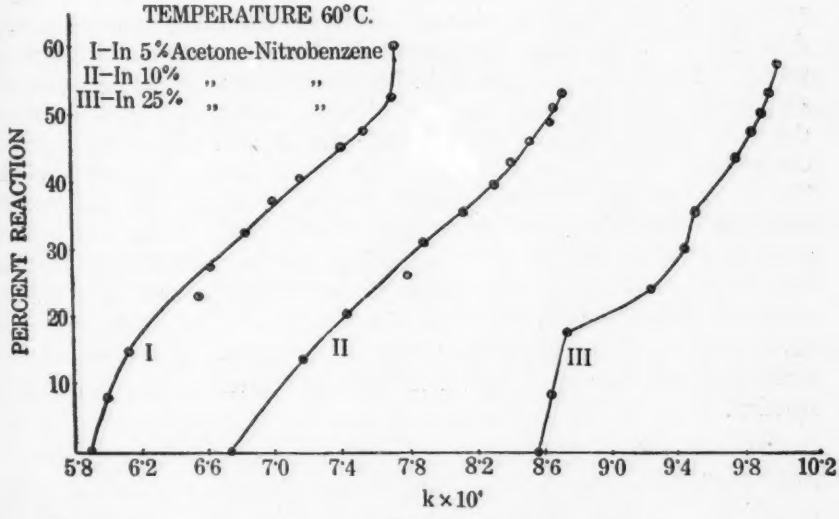

FIG. 2

the difference between the initial rate and the mean value of the rate constant followed the lines of the pure solvents but as will be considered later, the actual values and their variation are not without significance. It is also interesting to note that acetone-carbon tetrachloride mixture did not show any deviations in the rate constant.

Reliable values of the dielectric constants of the mixtures used in the present studies are not available but the results nonetheless show that the dielectric constant of the solvent as such is inadequate to account for the features. If one were to take only the rate constant into consideration, the initial addition of acetone to nitrobenzene causes an increase in rate with a maximum at about 25% acetone and this slowly falls off towards the value for pure acetone. The Arrhenius parameters, however, show that the trend is not so straightforward. The initial addition of acetone causes a reduction in the activation energy which then rises to a maximum and with increase in acetone concentration falls off again. The frequency factor follows the same trend. While the results generally show the need for a polar environment for the reaction, the highest values for activation energy and frequency factor are obtained with nitrobenzene if we exclude the value estimated for the acetone-carbon tetrachloride mixture. The results reported here confirm the indications noticed with the pure solvent that solvation of the transition state is a significant factor.

The values of the Arrhenius parameters given for the acetone-carbon tetrachloride mixture are estimates by trial and error using the rate equation, $k = PZe^{-E/RT}$ and taking into account the known parallelism between the parameters as shown by the trends in the other solvents. It has been observed already that the rate could not be studied in pure carbon tetrachloride as the reaction was extremely slow. While the addition of acetone improves the position, the reaction is still very slow and is measurable only at 60° C. This is by itself not a disadvantage since one can expect that the reaction does not proceed beyond the first stage of alkylation. With only a small proportion of acetone in the composition, the overall dielectric constant is low enough to exclude any mechanism which presupposes the ionisation of the alkyl iodide as the first stage of the reaction.[3] This is borne out by the constancy of the bimolecular rate constant and the values of the Arrhenius parameters also conform to what one can expect for a bimolecular reaction.

The cause for a fair constancy in 95% ethyl alcohol-water system has to be attributed to the ability of the solvent to facilitate the removal of the proton in a solvated condition from the transition state, solvation of the

proton being easier and giving a more stable product than the alkyl ion. The intervention of a second molecule of aniline for the proton removal thus becomes unnecessary in this solvent.

The observed differences between nitrobenzene and acetone can be partly accounted for by the possibility that solvation of the proton by association with the carbonyl group of the ketone is easier than that with the nitro group. The behaviour of the mixed solvent, however, cannot be explained on this ground alone. In dealing with the reaction between dimethyl-aniline and methyl iodide, Edwards[4] considered that the rate of crystallisation would be the deciding factor. While this may be one of the factors where there was separation of some product of the reaction, in the acetone-nitrobenzene mixtures used in the present work, the reaction has been strictly homogeneous. Changes in the slope of the rate constant-percentage reaction curve are more definite than with the pure solvents, but the initial rate can be safely taken to represent the alkylation of the first hydrogen atom.

A comparable work is that of Muchin and coworkers[5] who studied the reaction between benzyl bromide and triethyl amine in benzene-nitrobenzene mixtures where a complex formation involving solvent is postulated. It is, perhaps, preferable to consider that the low values of the parameters are more consistent with the views that the transition state involves a solvated activated complex with the solvent providing a more favourable path for the reaction (*cf.* Ogg and Rice[6]; Wynne-Jones and Eyring[7]). An indication that there is some kind of interaction is that in contrast to the very pale colour of nitrobenzene and of the reactants, the solutions are invariably of a bright brown colour. The final product is also colourless.

It was observed in the previous part[1] that alkylation of aniline is analogous to the formation of the quaternary ammonium compound, the rupture of the N–H bond forming a subsequent or simultaneous step. The justification for such a picture is well brought by a comparison of solvent influence on the reaction rate in the two reactions (*vide* Table III).

The similarity between the two is brought out even better by comparing the data indicated by Laidler and Hinshelwood[12] and the present work with solvent mixtures. This is illustrated in Fig. 3.

In solvents, rich in the proportion of acetone, the general trend appears to be the same, but, in the initial addition of acetone to nitrobenzene, pronounced differences appear. In the course of studies in ester hydrolysis,

TABLE III

Activation energies and solvent influence

Reaction	Solvent		
	Nitrobenzene	Acetone	95% Ethyl alcohol
Aniline-bromo-acetophenone[8] ..	13·5	11·1	13·9
Aniline-methyliodide[1]	16·83	13·23	15·37
Dimethylaniline-methyliodide[9] ..	13·17	..	..
Pyridine-methyliodide	13·60[10]	11·28[11]	17·82[11]
Pyridine-benzyl bromide[5] ..	8·4		14·3

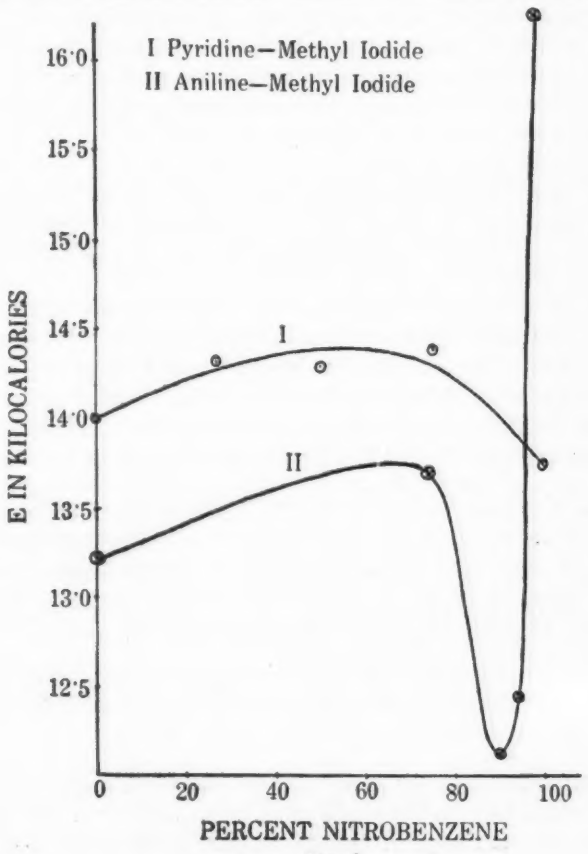

FIG. 3

it appeared that initial additions of acetone or dioxan to water caused deviations from the commonly accepted picture correlating the influence of dielectric constant on the reaction.[13] This abnormality has been further substantiated by work with the initial parts of the curves.[14] As abnormalities appeared to be possible in the region of small additions, the present work on solvent mixtures has been initially in this region. With the following picture of the reaction:

$$1\,a.\quad \begin{cases} \text{(i)}\ MeI \xrightarrow{\text{fast}} Me^+ + I^- \\ \text{(ii)}\ C_6H_5NH_2 + Me^+ \xrightarrow{\text{slow}} [C_6H_5NH_2Me]^+ \end{cases}$$

$$1\,b.\quad C_6H_5NH_2 + MeI \longrightarrow [C_6H_5NH_2Me]^+ + I^-$$

$$2.\quad [C_6H_5NH_2Me]^+ \rightleftharpoons C_6H_5NHMe + H^+$$

the second stage involves proton removal and acetone is probably more efficient molecule than nitrobenzene in this respect. The lowered activation energy indicates that the rate determining step leads to a transition state suitably aligned with respect to the component solvents, 10% acetone constituting, probably, a limiting composition. Both Arrhenius parameters have the smallest value in this solvent.

It is generally considered that, where a product is highly polar, the transition complex needs a highly polar environment to fix it. In the present reaction hydrogen halide or the solvated proton is the only highly polar product while the original and the alkylated amine are of comparable polarity. This means that, the formation of the transition state needs a polar environment as is found to be the case, but the formation of the product can be either by the original amine or by the intervention of the solvent. The formation of the 'Onium Compound does not involve the intervention of the solvent for the final product except for providing a polar environment but in the alkylation of aniline, the solvent can be an active participant by intervention in proton removal. This essential difference can account for the observed features of the two curves.

Experimental

The experimental details were as in the previous part.[1] The reactions were carried out in large electrically controlled thermostat and the course of the reaction followed by estimations of the iodide formed in the course of the reaction. Typical runs are given in Tables IV–V (Figs. 4 and 5) below;

TABLE IV

The reaction in mixed solvents at 50° C.

Solvent	Concentration of aniline	Concentration of methyl-iodide	Strength of silver nitrate	Typical run
5% Acetone-nitrobenzene ..	0·09750*	0·1082*	0·02444 N	A
10% ,, ..	0·09774*	0·1082*	0·02444 N	B
25% ,, ..	0·09804*	0·1065*	0·02444 N	C

A	Time in minutes	60	120	180	240	300	360	420
	Titre value	4·60	8·70	12·40	15·35	17·70	20·25	22·20
B	Time in minutes	60	120	180	240	300	360	420
	Titre value	5·20	9·70	13·65	16·60	19·10	21·30	23·00
C	Time in minutes	35	80	125	185·4	245	305	365
	Titre value	3·75	8·10	11·18	15·50	18·50	20·95	22·75

* Concentration in mol./l.

TABLE V

Reaction in mixed solvents at 60° C.

Solvent	Concentration of		Strength of silver nitrate	Typical run
	Aniline (mol. per litre)	Methyliodide (mol. per litre)		
5% Acetone-nitrobenzene	0·09701	0·1070	0·02444 N	A
10% ,,	0·09729	0·1093	0·02588 N	B
25% ,,	0·09826	0·1077	0·02588 N	C
10% Acetone carbon tetrachloride	0·1000	0·1128	0·02588 N	D

A	Time in minutes ..	35	80	125	170	215	260	305
	Titre value	4·7	10·1	14·5	17·8	20·75	22·95	24·5 ml
B	Time in minutes ..	40	80	120	160	200	240	
	Titre value	6·05	11·15	15·1	18·1	20·6	22·45	ml
C	Time in minutes ..	40	80	120	160	200	240	
	Titre value	7·15	12·65	16·75	19·6	21·8	23·75	ml
D	Time in minutes ..	310	540	840	1260	1980	2999	ml
	Titre value	3·0	5·0	7·35	10·1	13·75	17·3	ml

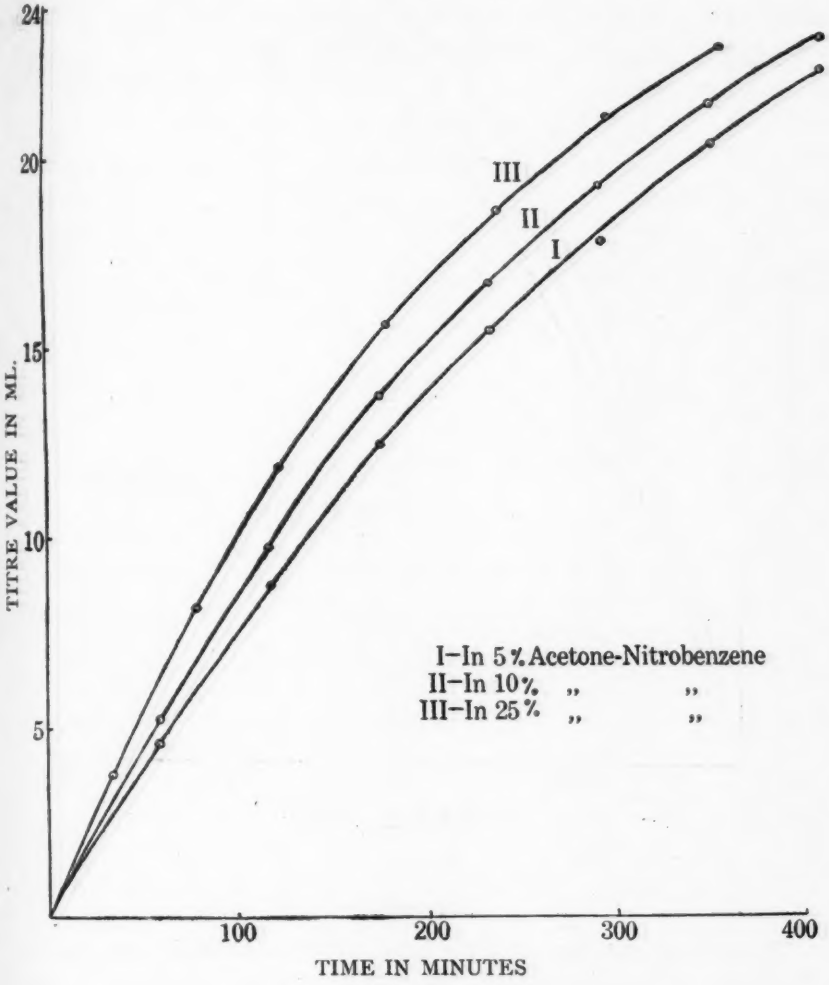
24
20
15
10
5
TITRE VALUE IN ML.
III
II
I
I–In 5% Acetone-Nitrobenzene
II–In 10% „ „
III–In 25% „ „
100
200
300
400
TIME IN MINUTES

FIG. 4

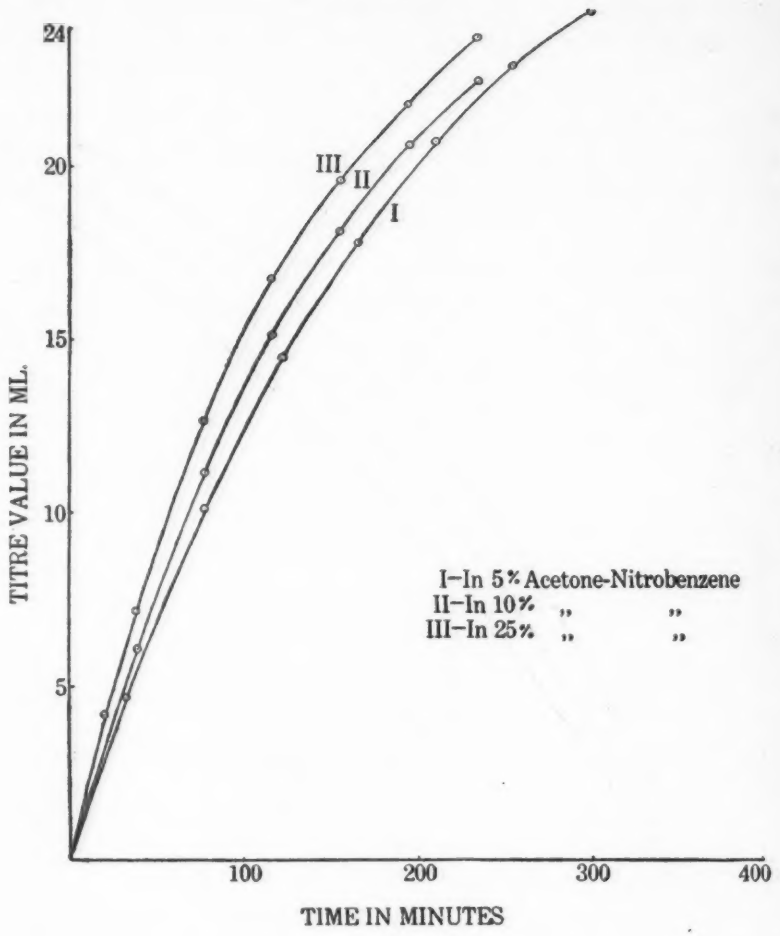

FIG. 5

SUMMARY

The previous part dealt with the kinetics of the reaction in pure solvents and it appeared desirable to study the reaction in mixed solvents. The present paper deals with a study in mixtures of acetone and nitrobenzene and one mixture of acetone and carbon tetrachloride, Acetone-nitrobenzene mixtures showed the same trend in the rate constants that was noticed with the pure solvents while the acetone-carbon tetrachloride mixture showed a

good bimolecular rate. The general influence of the solvent on the rate and the Arrhenius parameters are discussed.

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COMPARATIVE STUDIES OF ALTERNATING AND DIRECT CURRENT POLAROGRAPHY: EFFECT OF CONCENTRATION

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Introduction

The direct current polarography originally invented by Heyrovsky involves the study of the current voltage curves obtained when solutions containing electro-oxidisable or reducible substances in presence of a "base" or supporting electrolyte are electrolysed by dc potentials employing mercury dropping from a fine glass capillary as one of the electrodes[1]; the curves usually known as polarograms are *S*-shaped in nature and often spread over 0·2 to 0·3 volt. The polarograms follow a relationship[2]

$$E = E_{\frac{1}{2}} + \frac{0{\cdot}0591}{n} \log (i_d - i)/i \qquad (1)$$

where i is the current passing through the system at any applied dc potential E; i_d, the limiting current; $E_{\frac{1}{2}}$, the potential at which $i = i_d/2$; and n, the number of electrons involved in the reduction or oxidation occurrent at the dropping mercury electrode (d.m.e.). It is established that $E_{\frac{1}{2}}$ is characteristic of the electro-active substance, and i_d, a measure of the concentration thereof. These features formed the basis for qualitative detection and quantitative determination of a large number of inorganic and organic substances. A limitation of the dc polarography is however that analysis of a mixture of two or more substances is not possible when in a given supporting electrolyte, their half-wave potentials are not wide apart.

Mathematical analysis of equation (1) shows that the derivative di/dE is maximum at $E = E_{\frac{1}{2}}$; and that the value of di/dE at $E = E_{\frac{1}{2}}$ is proportional to i_d and therefore, to the concentration of the substance undergoing reduction or oxidation at the d.m.e. The curves representing the variation of di/dE will thus have peaks instead of "steps" or waves of the dc polarograms. Various attempts have been made to investigate experimentally the derivative polarograms. Heyrovsky[3] employed a system containing two dropping mercury electrodes dipping into one cell, while Semerano Riccobino used them immersed in two separate cells. The two dropping

electrodes were connected across an end resistance in the potentiometer bridge so that their potentials differ from one another by a constant quantity ΔE as the applied potential was gradually increased; the resultant Δi was indicated by a galvanometer. The main disadvantage of using two dropping electrodes has been that the drop times periodically go in and out of phase leading thereby to distortion in the derivative polarogram by the periodic variation in the magnitude of the current oscillations.

Recently Breyer *et al.*[4] used superimposition of a small ac voltage of a known frequency on the dc potential applied to d.m.e. The method known as the alternating current polarography is simple and involves the measurement at varied applied dc potentials, of the differential alternating current flowing through the system. By suitable adjustment of the magnitude of the superimposed ac voltage, this method provides a possibility of investigation of substances whose half-wave potentials differ only by 0·05 volt. Thus a mixture of Cd^{++} and In^{+++} with $-0{\cdot}610$ and $-0{\cdot}565$ volts *vs.* S.C.E. as their respective half-wave potentials could not be analysed by dc polarography, while by employing low superimposed ac voltages (V_{ac}; 5–10 millivolts), separate peaks due to the reduction at d.m.e., of Cd^{++} and In^{+++} could be recorded with the alternating current polarograph. At large values of V_{ac}, however, the two peaks coalesced; this was primarily due to the observed appreciable width or potential spread of the peaks at large V_{ac}.[5] Thus the voltage spread of the polarograms is of importance in controlling the polarographic analysis of substances. The present communication reports comparative studies of the variation with the concentration of an electro-reducible substance like Cd^{++}, of the wave-spread of direct and alternating current polarograms.

Experimental

The electric circuit employed by the present authors is shown in Fig. 1. Dc potentials were obtained by a Cambridge potentiometer (P) energised by a dry battery; the accuracy of their measurement was 0·001 volt. The exact potential E obtained by P was often checked up by a standard cell.

Alternating potentials of 50 cycles/sec. were obtained from ac mains of 220 volts. These were stabilised to be free from fluctuations by a Barratter assembly (G.E.C.) and stepped down to 8 volts. From this constant and low voltage, ac potentials in the range 5–100 millivolts were obtained by a suitable network of non-inductively wound wire-resistances. The amplitude of the ac voltage was verified by an oscillograph.

Dc potentials or those superimposed by a given ac voltage could be applied to d.m.e. by the operation of the switch S (Fig. 1); when this last

was put on to the position 1, dc potential of a desired value could be applied to d.m.e. through a resistor, R_1, while when S was turned to 2, the dc, together with the ac, voltage was applied to d.m.e. through a non-inductive non-capacitative resistor R_2. Measurement of the potential developed across R_1 (position 1) at different applied dc voltages E gave the dc polarograms. The alternating current flowing through the system was investigated as follows: With the switch S kept on to the position 2, the potential developed across R_2 was fed through a condenser C (Fig. 1) to an amplifier; the amplified voltage was rectified and measured by a potentiometer. This last was of Leeds and Northrup Company and was calibrated to give the potentials directly in volts. The accuracy of the instrument was 0·0005 volt which corresponded to 0·01 μamp.

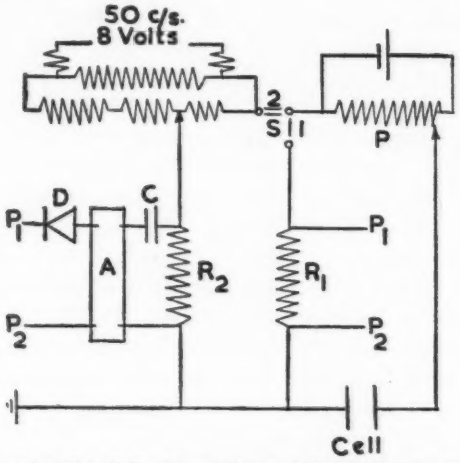

FIG. 1. Experimental Circuit for Alternating and Direct Current Polarography.
P_1 and P_2 lead to potentiometer (Leeds and Northrup); D = detector (1 N34); A = amplifier.

The dropping mercury electrode had the following characteristics: at a pressure of 32 cm. of mercury, the drop time (t) on open circuit in 0·1 M potassium chloride was 1·6 secs.; the weight of mercury dropping per sec. (m) was 2·5 mg.; and $m^{2/3}t^{1/6}$ was 1·99.

Cadmium sulphate of Merck quality was used; this was recrystallised several times in water and later dried at 160° C.

Potassium chloride of Analar grade was used.

RESULTS AND DISCUSSION

A typical series of alternating current polarograms obtained at different concentrations of Cd^{++} are given in Figs. 2 and 3; the data in Fig. 2 refer

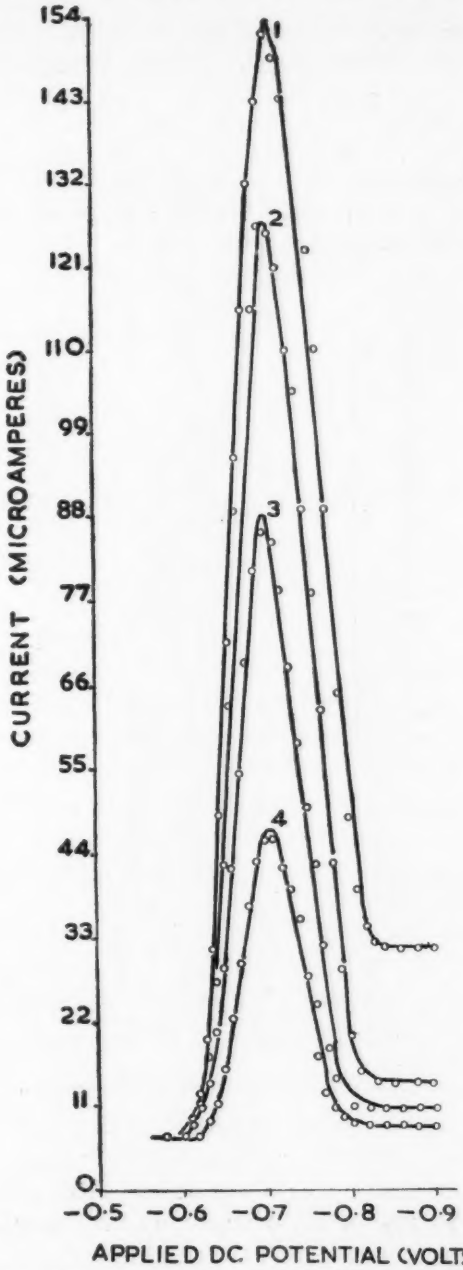

FIG. 2. Alternating Current Polarograms of Cd^{++} with Superimposed ac Voltage = 30 millivolts.

Curve 1 = 5 mM; 2 = 3 mM; 3 = 1 mM; and 4 = 0·5 mM of Cd^{++}.

to 30, and those in Fig. 3, to 10 millivolts used as the superimposed ac voltage, V_{ac}. For purposes of comparison, the corresponding dc polarograms

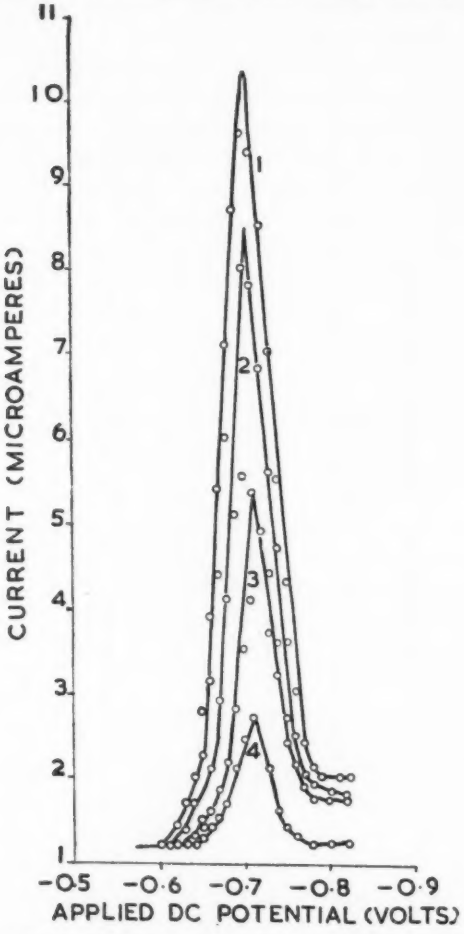

FIG. 3. Alternating Current Polarograms of Cd^{++} with Superimposed ac Voltage = 10 millivolt.

Curve 1 = 1·0 mM; 2 = 0·8 mM; 3 = 0·5 mM and 4 = 0·1 mM.

are returned in Fig. 4. These results (Figs. 2–4) were obtained without the addition of any maximum suppressor like gelatine; this last is not necessary since Cd^{++} does not show any polarographic maximum.[1] Further, the data were obtained in the presence of air; removal of this last by

bubbling purified nitrogen through the solution did not materially affect the polarograms except that the heights of ac peaks increased slightly.

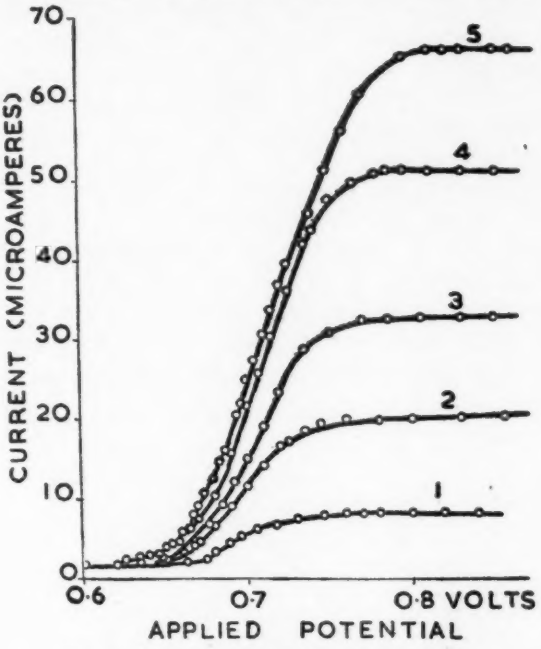

FIG. 4. Direct Current Polarograms of Cd^{++}.
Curve 1 = 1 mM; 2 = 3 mM; 3 = 5 mM; 4 = 8 mM and 5 = 10 mM.

It was interesting to note from the data in Figs. 2 and 3 that in 0·1 M potassium chloride solution as the supporting electrolyte, well-defined peaks were obtained in the alternating current polarography due to the reduction at d.m.e. of Cd^{++}. The summit potential (E_s) corresponded to $-0{\cdot}62$ volt *vs.* S.C.E.; this was equal to the recorded value of half-wave potential, $E_{\frac{1}{2}}$, of the dc polarograms (Fig. 4).[5] Further, E_s and $E_{\frac{1}{2}}$ were roughly unaltered by a change in the concentration of Cd^{++} especially in the range 0·5 to 10 mM. It is seen from Figs. 2–4 that the observation of E_s is comparatively simple and does not involve the measurement, as in the case of $E_{\frac{1}{2}}$, of i_d and the potential corresponding to $i_d/2$.

The data in Figs. 2 and 3 show that the peak value of the current i_s, corresponding to i_d of the dc polarograms, increases with a like change in the superimposed ac voltage. Thus, *e.g.*, at 1 mM concentration of Cd^{++}, i_s was approximately 10 and 85 μamps. with $V_{ac} = 10$ and 30 millivolts

respectively (Figs. 2 and 3). Further, i_s increased with an increase in the concentration of Cd^{++}. Thus, *e.g.*, i_s was 45, 85 and 150 μ amps. for 0·5, 1·0 and 5·0 mM of Cd^{++} (Fig. 2). Comparison of the data in Figs. 2 and 4 shows that *ceteris paribus* the current in the alternating polarography is about 8 times greater than the values recorded in dc polarography. Thus, *e.g.*, at 1·0 mM of Cd^{++}, i_s was approximately 80, while i_d was 8 μamps. The appreciably large values of the current in the ac polarography enables one to make measurements with relatively large accuracy. It may be further pointed out that the low impedence character stic of the alternating polarographic circuit necessitates the use of low resistance values for R_2 (450 ohms.; *cf.* R_1 used for dc polarography = 12,000 ohms). The results in Figs. 2–4 further show that while the current i_d increased sensibly linearly with the concentration up to 10 mM (see Curve 1, Fig. 5) the peak value of the current, i_s, in the alternating current polarography varied linearly up to 1·0 mM, tending to saturate at larger concentrations (Curve 2, Fig. 5).

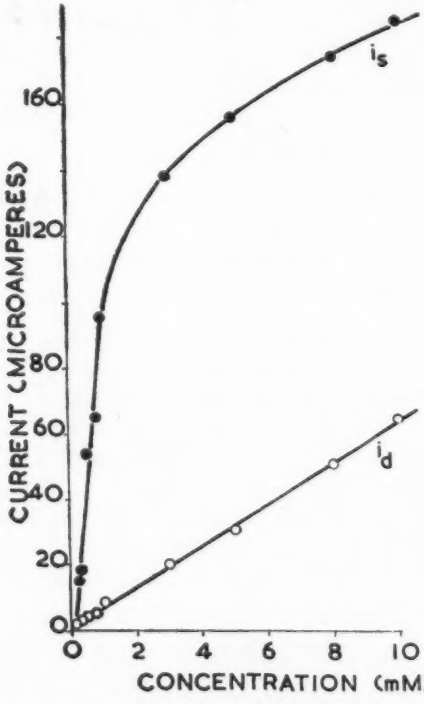

FIG. 5. Variation of Limiting Current (i_d) and Summit Current (i_s) with Concentration.

The results in Figs. 2–4 further show that the potential width of both the alternating and direct current polarograms is markedly dependent upon the concentration of the electro-reducible substance. It may be added that in considering the wave-spread of ac peaks (W_{ac}) (Figs. 2 and 3) the potential width of the polarograms corresponding to the current values half of the summit current i_s, has been taken into account. It can be shown that at a given molar concentration, when the difference between W_{ac} of two components is greater than the difference between their half-wave potentials, the mixture of the two substances can be analysed by the alternating current polarography; *i.e.*, two separate ac peaks at the respective half-wave potentials can be recorded. It was interesting to note from the data in Fig. 6 *a* that the wave-spread in ac polarography is less than that in dc polarography especially in the range of concentration 1–10 mM of Cd^{++}. Thus, *e.g.*, at 5·0 mM of Cd, W_{ac} was 0·11 (with $V_{ac} = 30$ millivolts), while the wave-width (W_{dc}) of the dc polarogram was 0·22 volt. The curve representing the variation of W_{ac} with concentration was below that showing

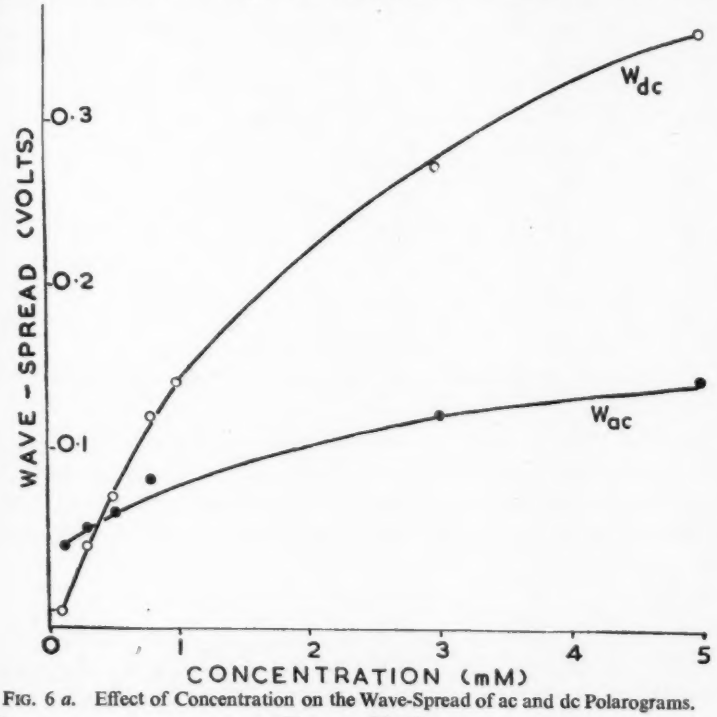

FIG. 6 *a*. Effect of Concentration on the Wave-Spread of ac and dc Polarograms.

A3 V_{ac} = 30 mV.

the relationship between W_{dc} and the concentration of the substance (Fig. 6 *a*).

The low values of W_{ac} point out one of the advantages of the ac polarography over the dc polarography, as the analysis of two components with their half-wave potentials close to each other, becomes feasible with the ac polarography. With concentrations of Cd^{++} less than 1 mM, W_{ac} with 30 millivolts as the superimposed ac voltage was greater than W_{dc} (see Curves 1 and 2, Fig. 6 *a*) indicating that use of dc polarography would be advantageous for low concentrations such as 0·1 to 0·5 mM; it may be pointed out that the corresponding current values which are usually of the order of a microampere or a fraction thereof, set a limitation to the accuracy of the measurements; besides, at these low concentrations, the appreciable rate of change of *condenser current* with applied voltage leads to the development of ill-defined waves, which results in inaccurate analysis of i_d, etc. The results obtained with 10 millivolts as superimposed ac voltage (Fig. 6 *b*)

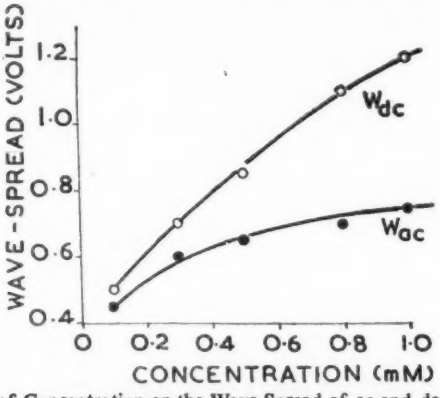

FIG. 6 *b*. Effect of Concentration on the Wave-Spread of ac and dc Polarograms. V_{ac} = 10 mV

show that even at low concentrations such as 0·1 mM Cd^{++}, W_{ac} is smaller than W_{dc}, indicating that analysis of a mixture of two components with close half-wave potentials at such small concentrations can be satisfactorily carried out on ac polarography using low values of the superimposed ac voltages.

SUMMARY

Alternating and direct current polarograms of Cd^{++} at different concentrations in the range 0·1 to 10 mM were recorded using 0·1 M potassium chloride solution as the supporting electrolyte. While the diffusion current

i_d in dc polarography increased linearly with concentrations up to 10 mM, the summit current i_s at $-0{\cdot}62$ volts *vs.* S.C.E. (the half-wave potential of Cd^{++}) increased linearly up to 1 mM tending to saturate at larger concentrations. The potential width of the ac peaks was lower than the corresponding dc wave-spread indicating that analysis of a mixture of two components with their half-wave potentials close to each other, was possible in the ac polarography.

ACKNOWLEDGEMENT

Authors' grateful thanks are due to Professor K. S. G. Doss, D.SC., F.R.I.C., F.A.SC., F.INST.P., Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest in the work, and to the Ministry of Education, Government of India, for granting a fellowship to one of us (S. K. D. Agarwal).

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SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

Part XXXII. A Synthesis of Tectorigenin

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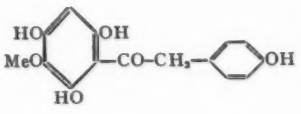
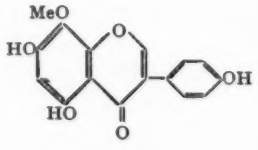
Out of thirteen isoflavones so far isolated from plants, only three (muningin, tectorigenin and irigenin) are known to have hydroxyl or methoxyl groups in the 5: 6: 7-positions. Muningin, which is 6: 4′-dihydroxy-5: 7-dimethoxyisoflavone, has been synthesized by us,[1] and we are now reporting the synthesis of tectorigenin, 5: 7: 4′-trihydroxy-6-methoxyisoflavone.

From the rhizomes of *Iris tectorum* Shibata isolated aglucoside, tectoridin, which on hydrolysis gave glucose and an aglucone, tectorigenin.[2] Tectoridin also occurs in the root of *Belamcanda chinensis* (L.) Leman.[3] Shibata[2] showed that tectorigenin contained one methoxyl and three hydroxyl groups, forming a triacetate and a tribenzoate, but he was able to prepare only a dimethyl ether. Alkaline hydrolysis yielded formic acid, iretol and *p*-hydroxyphenylacetic acid. Shibata suggested a 3-coumaranone structure for tectorigenin. Subsequently Asahina, Shibata and Ogawa,[4] on the basis of the similarity between irigenin and tectorigenin and of the absorption spectra, assigned the isoflavone structure (I).

No successful synthesis of tectorigenin has yet been described, but the 7: 4′-dimethyl ether,[5] 5: 7: 4′-trimethyl ether,[1, 6] and 5: 7: 4′-triethyl ether[6] have been synthesized. Baker *et al.*[7] tried to cyclize the ketone (II) to tectorigenin by their method of ethoxalylation, but the product was the isomer (III).

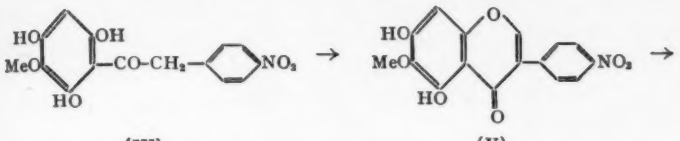


(II)

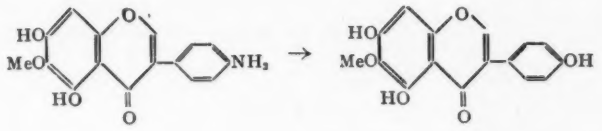


(III)

Tectorigenin has now been synthesized by the following route, which is similar to that employed for the synthesis of prunetin.[8]

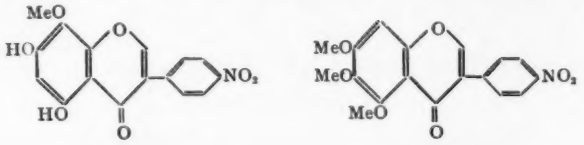


(IV) (V)



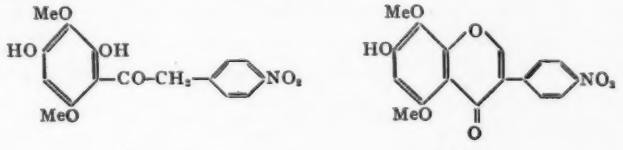
(VI) (I)

2: 4: 6-Trihydroxy-3-methoxyphenyl 4-nitrobenzyl ketone (IV), m.p. 220°, was prepared from iretol and *p*-nitrobenzyl cyanide by the Hoesch reaction. The ketone on cyclization with ethyl orthoformate[9] in pyridine-piperidine gave 5: 7-dihydroxy-6-methoxy-4′-nitroisoflavone (V), m.p. 307° (*decomp.*). The fact that cyclization of the ketone (IV) proceeded in the desired direction to give the isoflavone (V), and not the isomer (VII), has been confirmed by methylating it with dimethyl sulphate and potassium carbonate in acetone; the product, m.p. 233°, was 5: 6: 7-trimethoxy-4′-nitroisoflavone (VIII), since

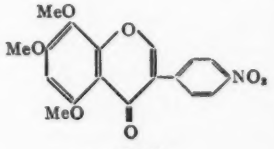


(VII) (VIII)

it was different from 5: 7: 8-trimethoxy-4′-nitroisoflavone (IX), m.p. 181°. The latter substance was prepared by a series of reactions which indicated its structure (IX) without ambiguity.



(X) (XI)



(IX)

2:5-Dimethoxyresorcinol was condensed with *p*-nitrobenzyl cyanide by the Hoesch reaction. The resultant ketone (X), m.p. 174°, gave on cyclization with ethyl orthoformate the isoflavone (XI), m.p. 312° (*decomp.*), methylation of which by the acetone-potassium carbonate method, yielded 5:7:8-trimethoxy-4′-nitroisoflavone (IX), m.p. 181°.

Ethyl orthoformate cyclization of deoxybenzoins having a free phloroglucinol nucleus usually leads to polymeric red products.[10] However, 2:4:6-trihydroxyphenyl 4-nitrobenzyl ketone has been cyclized to the corresponding isoflavone[11] with ethyl orthoformate, pyridine and piperidine in a yield of 12%. The ketone (IV), which has a methoxyphloroglucinol (iretol) nucleus, underwent the ethyl orthoformate cyclization more smoothly, the yield of isoflavone being 25 per cent.

Reduction of 5:7-dihydroxy-6-methoxy-4′-nitroisoflavone (V) with zinc and acetic acid gave 5:7-dihydroxy-6-methoxy-4′-aminoisoflavone (VI), m.p. 221° (*decomp.*). Diazotization of the amine (VI) and hydrolysis with boiling 48% sulphuric acid yielded a substance, which after passage of the solution in ethyl acetate through a short column of Florex and crystallization of the material recovered from the percolate led to very pale yellow needles, m.p. 227°, not depressed by mixing with natural tectorigenin. The synthetic isoflavone gave a green ferric colouration like the natural substance. The triacetate of (I) melted at 190–91°, not depressed by mixing with the triacetate prepared from natural tectorigenin.

EXPERIMENTAL

2:4:6-*Trihydroxy*-3-*methoxyphenyl* 4-*nitrobenzyl ketone* (*IV*)

A suspension of iretol (8 g.), *p*-nitrobenzyl cyanide (8 g.), and fused zinc chloride (8 g.) in dry ether (200 c.c.) was saturated with dry hydrogen chloride at 0°. The reaction mixture was kept in an ice-chest for 48 hours. The ether was decanted off and the red oily ketemine hydrochloride was washed twice with dry ether. The oil was then refluxed for 5 hours with water (300 c.c.) containing a few c.c. of conc. hydrochloric acid. The mixture was cooled and the solid which separated was treated with a solution of sodium carbonate. The dark red solution was filtered and acidified with conc. hydrochloric acid. The solid which separated (7·8 g.) crystallized from 95% alcohol in pale brown needles, m.p. 220° (Found: C, 56·2; H, 4·4; N, 4·4. $C_{15}H_{13}O_7N$ requires C, 56·4; H, 4·1; N, 4·4%). The substance gives a brown colouration with alcoholic ferric chloride.

5:7-*Dihydroxy*-6-*methoxy*-4′-*nitroisoflavone* (*V*)

The ketone (IV) (2 g.), dry pyridine (16 c.c.), piperidine (1 c.c.) and redistilled ethyl orthoformate (10 c.c.) were refluxed for 8 hours, and the

solution left in a refrigerator for 12 hours. The solid which separated crystalized from glacial acetic acid in prisms (0·5 g.), m.p. 307° (*decomp.*) after darkening at 290° (Found: C, 58·8; H, 3·7; N, 4·1. $C_{16}H_{11}O_7N$ requires C, 58·4; H, 3·4; N, 4·2%). The substance gives a yellowish green colouration with alcoholic ferric chloride.

5:6:7-*Trimethoxy-4'-nitroisoflavone* (*VIII*)

The isoflavone (V) (0·1 g.) was suspended in dry acetone (20 c.c.) and treated with dimethyl sulphate (0·3 c.c.) and freshly ignited potassium carbonate (1 g.). After refluxing for 12 hours, the acetone solution was filtered, and the residue extracted with 20 c.c. of dry acetone. The acetone solution was concentrated and water was added. The solid which separated crystallized from dilute acetone in pale yellow feathery needles, m.p. 233° (Found: C, 60·4; H, 3·9; N, 3·9. $C_{18}H_{15}O_7N$ requires C, 60·5; H, 4·2; N, 3·9%).

4'-*Amino*-5:7-*dihydroxy*-6-*methoxyisoflavone* (*VI*)

The isoflavone (V) (0·2 g.) and zinc dust (0·4 g.) were suspended in boiling 95% alcohol (40 c.c.), and glacial acetic acid (4 c.c.) was added in four portions at intervals of 30 minutes. After refluxing for 30 minutes longer, the solution was filtered hot, the filtrate concentrated to 5 c.c. and diluted with water. The precipitate thus obtained was collected and dissolved in chloroform. The chloroform solution was then saturated with dry hydrogen chloride, the pale pink coloured precipitate of the amine hydrochloride was filtered, triturated with sodium bicarbonate solution, left overnight, and filtered. The residue crystallized from alcohol in irregular plates. After drying at 110° for 4 hours over phosphorous pentoxide at 2 mm. pressure, it melted at 221° (*decomp.*) with shrinking at 214° (Found: C, 64·5; H, 4·6; N, 4·3. $C_{16}H_{13}NO_5$ requires C, 64·2; H, 4·4; N, 4·7%). The substance gives a brownish green colouration with alcoholic ferric chloride.

Tectorigenin (*I*)

The amine (VI) (0·16 g.) was suspended in a mixture of water (8 c.c.) and conc. sulphuric acid (1·6 c.c.). The mixture was cooled in ice and treated with a cooled solution of sodium nitrite (0·07 g.). After allowing the mixture to stand at 0° for 30 minutes, the excess nitrous acid was destroyed by the addition of urea. The diazonium solution was gradually poured into a boiling mixture of water (16 c.c.) and conc. sulphuric acid (8 c.c.). The solution was boiled till no red colouration was obtained with β-naphthol in aqueous alkali (3–4 mins.). The solution was cooled, diluted

with water, and left overnight at room temperature. The solid was collected and extracted with boiling ethyl acetate. The ethyl acetate extract was run through a short column of Florex XXX. The pale yellow percolate was collected and the solvent removed by distillation. The solid thus obtained crystallized from alcohol or a mixture of ethyl acetate and *n*-hexane in very pale yellow flat needles, m.p. 227° (Found: C, 63·7; H, 4·2. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0%). The m.p. was not depressed by mixing with natural tectorigenin, kindly supplied by Professor Shibata. Tectorigenin has been stated in the literature[2, 3] to melt at 227° and at 230° (*decomp.*). The synthetic substance gives a green colouration with alcoholic ferric chloride.

The *triacetyl* derivative, prepared in the usual manner, crystallized from a mixture of ethyl acetate and *n*-hexane in colourless prisms, m.p. 190–91° after softening at 187° (Found: C, 61·7; H, 4·5. $C_{22}H_{18}O_9$ requires C, 62·0; H, 4·3%). The mixed m.p. with the acetyl derivative prepared from natural tectorigenin was not depressed. Shibata[2] cites m.p. 187° and Mannich *et al.*[3] cite m.p. 190° for tectorigenin triacetate.

2: 4-*Dihydroxy*-3: 6-*dimethoxyphenyl* 4-*nitrobenzyl ketone* (*X*)

The Hoesch reaction was carried out in the usual manner on 2: 5-dimethoxyresorcinol (4 g.), *p*-nitrobenzyl cyanide (4 g.), fused zinc chloride (1 g.) and dry ether (50 c.c.). The product crystallized from alcohol in pale brown plates, m.p. 174° (Found: C, 57·4; H, 4·5; N, 4·3. $C_{16}H_{15}O_7N$ requires C, 57·6; H, 4·5; N, 4·2%). It gives a deep red colouration with alcoholic ferric chloride.

7-*Hydroxy*-5: 8-*dimethoxy*-4′-*nitroisoflavone* (*XI*)

The ketone (X) (1·4 g.) was dissolved in dry pyridine (15 c.c.) and the solution was refluxed with ethyl orthoformate (15 c.c.) and piperidine (1 c.c.). After refluxing for 30 minutes separation of a solid occurred. After cooling, the precipitate (0·7 g.) was collected and crystallized from glacial acetic acid. The pale yellow needles had m.p. 312° (*decomp.*) after darkening at 297° (Found: C, 59·8; H, 3·6; N, 4·1. $C_{17}H_{13}O_7N$ requires C, 59·5; H, 3·8; N, 4·1%). The substance does not give any colour with ferric chloride.

5: 7: 8-*Trimethoxy*-4′-*nitroisoflavone* (*IX*)

The isoflavone (XI) (0·1) g.) in dry acetone (5 c.c.) was refluxed with anhydrous potassium carbonate (1 g.) and dimethyl sulphate (0·1 c.c.) for 12 hours. The product, worked up as usual, crystallized from dilute acetone in feathery needles, m.p. 181° (Found: C, 60·2; H, 4·3; N, 4·0. $C_{18}H_{15}O_7N$ requires C, 60·5; H, 4·2; N, 3·9%).

Summary

A synthesis of tectorigenin (5:7:4′-trihydroxy-6-methoxyisoflavone), which occurs as the 7-glucoside (tectoridin) in the rhizome of *Iris tectorum*, is described. 5:7-Dihydroxy-6-methoxy-4′-nitroisoflavone (V) was prepared by the action of ethyl orthoformate, pyridine and piperidine on 2:4:6-trihydroxy-3-methoxyphenyl 4-nitrobenzyl ketone (IV). The fact that cyclization of the ketone (IV) proceeded in the desired direction to give the isoflavone (V), and not the isomeric 5:7-dihydroxy-8-methoxy-4′-nitroisoflavone (VII), was shown by methylation, which yielded a substance different from 5:7:8-trimethoxy-4′-nitroisoflavone (IX); the latter (IX) was prepared by ethyl orthoformate cyclization of 2:4-dihydroxy-3:6-dimethoxyphenyl 4-nitrobenzyl ketone (X) to 7-hydroxy-5:8-dimethoxy-4′-nitroisoflavone (XI), followed by methylation. The nitroisoflavone (V) was reduced to the amine (VI), which was diazotized and treated with boiling sulphuric acid. 5:7:4′-Trihydroxy-6-methoxyisoflavone (I) thus obtained agreed in all its properties with natural tectorigenin.

Acknowledgment

We are greatly indebted to Professor S. Shibata, Pharmaceutical Institute, University of Tokyo, for a sample of natural tectorigenin, and to Dr. T. S. Gore for the microanalyses recorded in the paper.

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CHEMICAL INVESTIGATION OF INDIAN LICHENS*

Part XX. A New Synthesis of Teloschistin

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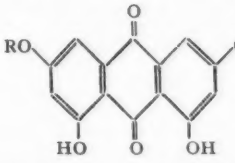
and Sankara Subramanian

(Department of Chemistry, Delhi University, Delhi, and Department of Pharmacy, Andhra University, Waltair)

Teloschistin was first isolated by Seshadri and Subramanian[1] from the Indian lichen *Teloschistes flavicans* Norm., and its constitution was established as 4 : 5-dihydroxy-7-methoxy-2-hydroxymethyl anthraquinone (I).[1, 2] In connection with the study of ω-hydroxy emodin (II), isolated from the mould *Penicillium cyclopium* Westling, Anslow *et al.*,[3] effected a partial methylation of it and the product was found to be identical with teloschistin.[2]



I, R = CH_3; R′ = OH
II, R = H; R′ = OH
III, R = CH_3; R′ = H

As an alternative method of synthesis, physcion (III) has now been used as the intermediate. The occurrence of physcion (III) and teloschistin (I) together in *T. flavicans* would indicate close biogenetic relationship. Physcion diacetate is converted into the corresponding ω-bromo derivative using N-bromo succinimide in carbon tetrachloride solution in the presence of benzoyl peroxide. This method has recently been used extensively by Seshadri and co-workers[4–7] for the synthesis of 2-hydroxymethyl chromones, -isoflavones, chromeno-chromones and 4-hydroxymethyl coumarins. Recently, Venkataraman *et al.*[8, 9] have also reported the use of this reagent for the conversion of rubiadin (1 : 3-dihydroxy-2-methyl anthraquinone) to the corresponding ω-hydroxy derivative, lucidin. In 2-methyl anthraquinones, the methyl group is reactive because of conjugation with the carbonyl group and hence is easily brominated with N-bromo succinimide. To avoid nuclear bromination, physcion (III) is converted into its diacetate (IV) which is subsequently brominated. The intermediate bromo derivative (V) is treated with silver acetate and acetic anhydride when teloschistin triacetate (VI) is obtained in satisfactory yield. Subsequent hydrolysis of the acetate with methanolic sulphuric acid gives teloschistin (I).

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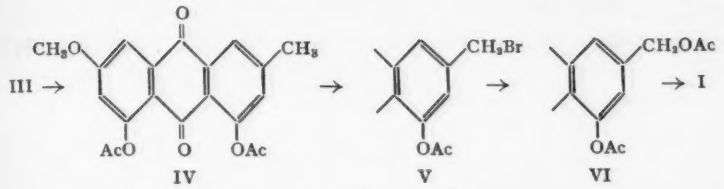
* A preliminary note was published in *J. Sci. Industr. Res. India*, 1954, **13 B**, 884.



The synthetic sample melts at 245–47° whereas natural teloschistin[1] was reported to melt at 229–30°. It was possible that the natural sample was slightly impure and hence had a lower melting point since it is known that, in anthraquinone derivatives, traces of impurities depress the melting points of the compounds considerably. Hence, natural teloschistin has been acetylated and subsequently deacetylated. It is found that the resulting purified sample melts at 244–6° and does not depress the m.p. of the synthetic sample. However, the possibility of two melting points of teloschistin (m.p. 229–30° and 245–47°) being due to dimorphism is not ruled out.

As a derivative of teloschistin, Seshadri and Subramanian[1] reported the preparation of teloschistin dimethyl ether using the dimethyl sulphate-acetone-potassium carbonate method. It is now found that methylation of teloschistin dimethyl ether with excess of methyl iodide and silver oxide in dry benzene solution, according to the method of Raistrick and Ziffer,[10] gives a trimethyl ether (m.p. 186–87°) and the melting point of this substance is the same as that of O-tetramethyl citreorosein, prepared by Posternak and Jacob[11] from citreorosein. Posternak[12] as well as Hind[13] claimed to have obtained the same substance by completely methylating 2-hydroxymethyl-4-methoxy-5: 7-dihydroxy anthraquinone (= roseopurpurin = carviolin) using dimethyl sulphate and aqueous alkali in acetone solution. But this method fails to give teloschistin trimethyl ether from teloschistin but yields only teloschistin 4: 5-dimethyl ether. A similar failure was also reported by Raistrick and Ziffer[10] who attempted the complete methylation of nalgiovensin (4: 5-dihydroxy-7-methoxy-2-hydroxypropyl anthraquinone) by this method.

Experimental Procedure

Synthesis of teloschistin

(i) *Bromination of physcion diacetate.*—To a solution of physcion diacetate[1] (m.p. 186–87°; 0·2 g.) in dry carbon tetrachloride (100 c.c.) were added freshly crystallised and dried N-bromo succinimide (0·15 g.) and benzoyl peroxide (0·02 g.) and the mixture refluxed on a water-bath for 24 hrs. The solution was then cooled in ice but no solid separated and hence the solvent was distilled off when a sticky yellow residue was left behind.

It was first washed with cold water twice and then with boiling water to remove the succinimide and unreacted NBS. The insoluble sticky solid was dried in a vacuum desiccator and directly used for the next stage. It gave a positive test for the presence of bromine.

(ii) *Conversion of the bromo derivative into the corresponding acetate.*—The above crude bromo compound (0·15 g.) was dissolved in acetic anhydride (5 c.c.) and silver acetate (0·5 g.) added. The mixture, after being refluxed in an oil-bath (150–60°) for 6 hrs., was poured into ice-water (200 c.c.) and stirred. The brownish yellow solid was filtered, washed with water and dried. It was boiled with benzene (4×50 c.c.), filtered to remove the silver bromide and the filtrate evaporated when a yellow solid was left behind which crystallised from ethyl acetate as lemon-yellow broad rectangular plates, m.p. 192–93°, identical with teloschistin triacetate. Yield, 0·1 g. It did not give any colour with alcoholic ferric chloride and did not answer the test for bromine.

(iii) *Hydrolysis to teloschistin.*—The above acetate (0·1 g.) was refluxed with a mixture of methyl alcohol (50 c.c.) and concentrated sulphuric acid (1·5 c.c.) on a water-bath for 45 mts. 2-Hydroxymethyl-4: 5-dihydroxy-7-methoxy anthraquinone crystallised from benzene as orange rectangular plates melting at 245–47°. Yield, 0·05 g. It was insoluble in aqueous sodium carbonate but dissolved in aqueous sodium hydroxide and potassium hydroxide giving a pink red solution. It gave a reddish brown colour with alcoholic ferric chloride (Found: C, 64·4; H, 3·8. $C_{16}H_{12}O_6$ requires: C, 64·0; H, 4·0 per cent.).

Hydrolysis of triacetate of natural teloschistin

Teloschistin triacetate[1] (m.p. 193°; 0·25 g.) was hydrolysed with a mixture of methyl alcohol (100 c.c.) and concentrated sulphuric acid (3 c.c.) as in the above case. The product crystallised from benzene as orange plates melting at 244–46°. Mixed melting point with the above synthetic sample was undepressed, and with the lower melting sample of teloschistin had a range (228-45°).

Teloschistin trimethyl ether

To a solution of teloschistin dimethyl ether[1] (0·25 g.) in dry benzene (75 c.c.) were added methyl iodide (20 c.c.) and dry silver oxide (3 g.). After refluxing the mixture for 2 hrs., more of methyl iodide (10 c.c.) and silver oxide (2 g.) (1 g. each time at the end of the first and second hour) were added. The refluxing was continued for 8 hrs. more and the mixture filtered off and the residue washed repeatedly with boiling benzene. The benzene solution

was concentrated to a small volume (about 10 c.c.) under reduced pressure. A yellow crystalline solid (0·2 g.) separated which was filtered off and crystallised from ethyl acetate when it was obtained as lemon-yellow needles, m.p. 185–86° (Found: C, 66·4; H, 5·4; OCH_3, 34·6. $C_{15}H_6O_2$ $(OCH_3)_4$ requires: C, 66·7; H, 5·2; OCH_3, 36·2 per cent.). Hind[13] reported a melting point of 186° for carviolin trimethyl ether and Posternak[12] reported a melting point of 187° for tetramethyl citreorosein (trimethyl roseopurpurin).

Teloschistin tribenzoate

Teloschistin (0·2 g.) was benzoylated using benzoyl chloride (1·5 c.c.) and pyridine (2 c.c.) and heating for 1 hr. on a boiling water-bath. The benzoate was worked up as usual and crystallised from ethyl acetate when it was obtained as yellow needles. m.p. 230–31°. Yield, 0·2 g. It was insoluble in cold aqueous sodium hydroxide (2%) and did not give any ferric chloride colour (Found: C, 72·1; H, 4·1; $C_{37}H_{24}O_9$ requires: C, 72·5; H, 3·8 per cent.).

Summary

Teloschistin has been prepared from physcion, the essential stage being the ω-bromo compound obtained by the use of N-bromo-succinimide. The higher m.p. of 244–46° is now recorded both for the synthetic and for the natural sample purified through the acetate. Complete methylation of teloschistin requires the use of methyl iodide and silver oxide at the final stage.

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STUDIES ON THE KINETICS OF THE SALT EFFECTS ON THE DECOMPOSITION OF MUREXIDE IN ACID SOLUTIONS

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In the previous communication,[1] it has been reported that murexide or ammonium salt of purpuric acid undergoes hydrolysis in acid solutions to give rise to uramil and alloxan; and that the kinetics of the reaction can be followed spectrophotometrically by studying the absorption at $\lambda = 530\ m\mu$. Further as in the case of inversion of sucrose in acid solutions,[2] the decomposition of murexide appeared to be first order in nature; and, the first order rate constant k was affected markedly by the concentration of the reacting substance. The first order rate constant of the inversion of cane sugar is influenced by the nature of the anion of the varied strong acids of the same concentration used, and also by neutral salts.[2] It is therefore, of interest to investigate the effect, if any, of the anion of the acids and salts on the first order rate constant of the decomposition of murexide; the present communication reports the results of this investigation.

Experimental

Murexide of B.D.H. quality was purified in the manner described earlier.[1] The other materials used were as follows: The hydrochloric acid used was of B.D.H. Analar quality. The hydrobromic acid was Merck sample and was free from bromine; the absence of this last was confirmed by testing with potassium iodide and starch. The nitric acid used was C.P. analysed product of Basic Synthetic Chemicals Ltd., and was of 99·9% purity.

The salts used were all Merck Analar samples.

All the reaction solutions containing acids and as well as salts were standardised by titration against Analar sodium carbonate.

The hydrolysis of murexide by different acids was investigated as follows: A known volume of the acid solutions was mixed with a fixed volume of murexide solution of a desired strength; the absorption, at $\lambda = 530\ m\mu$ of the reaction mixture, was studied at different intervals of time.

The effect of neutral salts on the hydrolysis of murexide was studied in the presence of only one acid, *viz.*, HCl. The reaction mixtures were so prepared that the final volume was the same containing fixed quantities (moles/litre) of the murexide and the acid but varying amounts of the salt, *viz.*, KCl, KBr, KI or KNO_3. Again the absorption at $\lambda = 530\ m\mu$ of the system was noted at varied intervals of time.

Results and Discussion

Figs. 1 and 2 give typical series of results on the time variation of optical density of the reaction mixtures containing different concentrations of two

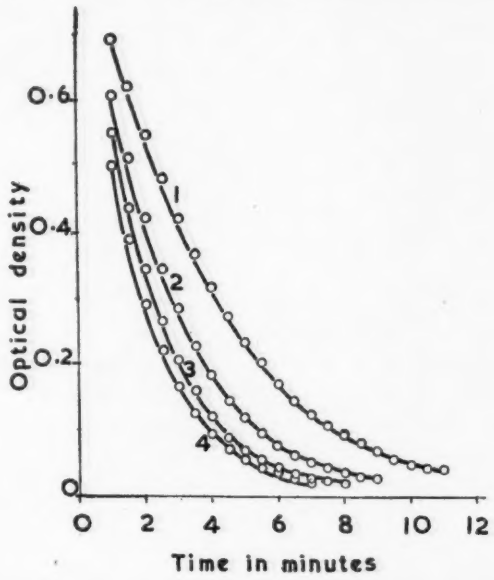

Fig. 1. Variation of optical density with time during the decomposition of murexide in hydrobromic acid solution.

Initial concn. of murexide = 0·25 mM; Temp. = 30° C., curve 1 refers to 4 mM; 2, to 6 mM; 3, to 8 mM; and 4, to 10 mM of HBr.

strong acids, HBr and HNO_3. As pointed out in the earlier communication,[1] the optical density decreased progressively with time; it was accompanied by the disappearance of the characteristic pink-red colour of murexide. The velocity constant k of the reaction was calculated by the application, to the data in Figs. 1 and 2, of the following formula:

$$\log (r' - r) = a - kt. \qquad \text{(i)}$$

Here r is the reading of the optical density at time t; r' is the same at $t + \tau$, where τ is a suitably chosen constant interval of time; and a, a constant. The applicability of this modified equation of a first order reaction requires

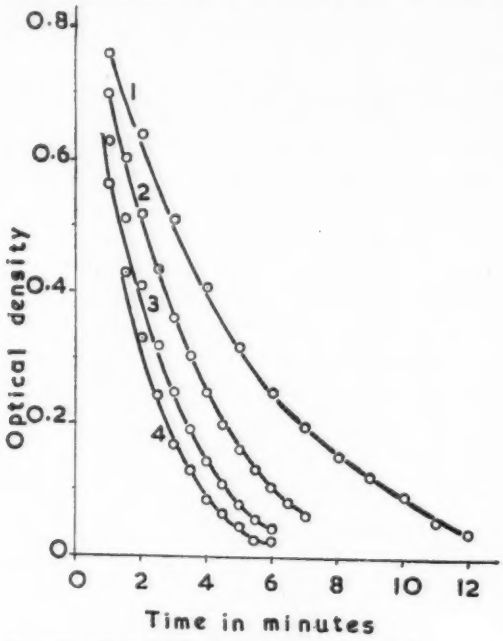

FIG. 2. Variation of optical density with time during the decomposition of murexide in nitric acid solution.

Initial concn. of murexide = 0·25 mM ; Temp. = 30° C.; curve 1 refers to 3 mM ; 2, to 5 mM ; 3, to 7 mM ; and 4 to 9 mM of HNO_3.

a linear variation of log $(r' - r)$ with t. This was demonstrated, in the previous communication,[1] by the sensibly linear plots obtained when log $(r' - r)$ was plotted against t. According to the eq. (i), the slope of the lines gives the values of k. Fig. 3 gives the values of k for different concentrations of the three strong acids studied, *viz.*, HCl, HBr and HNO_3. It was interesting to note that with increase in the concentration of the acid or the hydrogen-ion concentration, the velocity constant k increased progressively. Thus *e.g.*, k was 3·9, 15·3 and $26{\cdot}6 \times 10^{-6}$ min.$^{-1}$ at 1·0, 5·0 and 10·0 mM of HNO_3; the values of pH of the solutions were respectively 3·20, 2·48 and 2·15. Further, for a fixed concentration of murexide, the velocity constant was linearly variant with the concentration of the acid (see Fig. 3). It is interesting to note from the data in Fig. 3 that the values

of k for different concentrations of the three acids fall, within experimental errors, on the same straight line. The data appear to obey the following equation.

$$k/\text{min.}^{-1} = 2{\cdot}56 \times 10^{-3}\, C \qquad \text{(ii)}$$

where C represents the molar concentration of the acid. It was instructive to refer to the results on the effect of strong acids on the velocity constant k_1 of the inversion of sucrose: in this case also, k_1 is variant with the concentration of the strong acids; the variation of k_1 with C is represented by the following relationship:

$$k_1/\text{min.}^{-1} = 6{\cdot}95 \times 10^{-3}\, C \times 10^{B_j C}$$

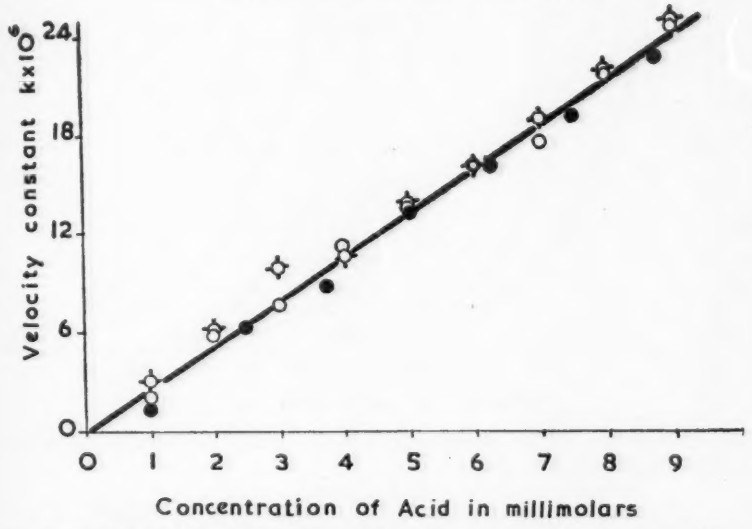

FIG. 3. Variation of the velocity constant k with the concentration of strong acids.
Concn. of murexide 0·25 mM ; Temp. 30° C.
○ KCl ; • HBr ; and -⊙- HNO_3.

Where B_j is a constant determined by the anion and is as follows:

$$Cl^- = 0{\cdot}28;\ Br^- = 0{\cdot}35 \text{ and } NO_3^- = 0{\cdot}30.$$

This observation, when analysed on the principle of specific interaction of ions, due to Brönstead, indicated the significant influence of the anions of the acids on the *reaction complex* involved in the inversion of sucrose, which has a single positive charge.[2] In the present series of experiments on the hydrolysis of murexide, however, the data in Fig. 3 especially the linear plot, k *vs.* C, indicate that the value of B_j is zero for all the anions

of the acids employed, suggesting thereby that the anion has no specific, significant role in the mechanism responsible for the decomposition of murexide. This is substantiated by the large amount of data obtained with mixtures of acid and salt solutions of varying concentrations. Fig. 4 gives a typical set of results on the time variation of the optical density of

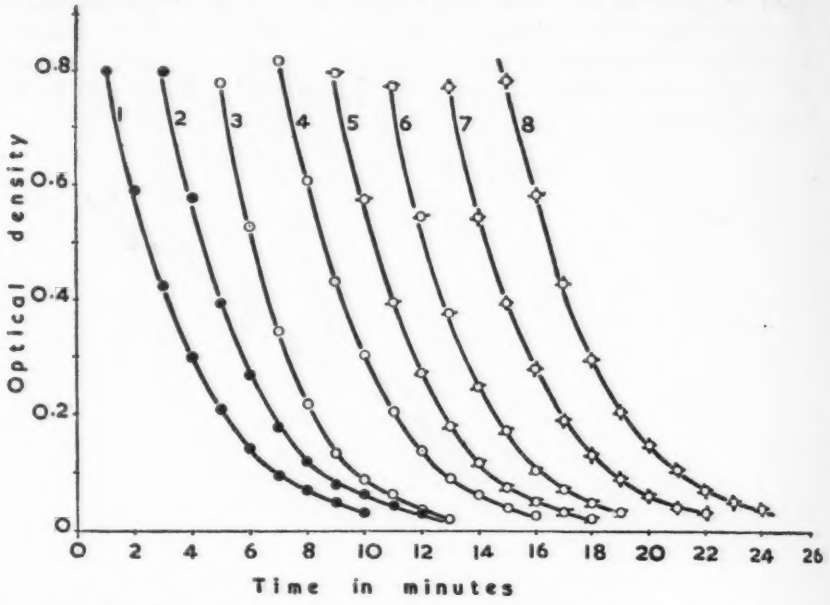

FIG. 4. Variation of the optical density with time during the decomposition of murexide in presence of HCl and neutral salts.

Curves 1 and 2—KCl ; Curves 3 and 4 KBr.
Curves 5 and 6—KI and Curves 7 and 8—KNO_3.

The scale on the abscissa refers to Curve 1. All the other curves start at 1 min. interval and their scale on abscissa have been shifted from the scale of Curves 1 by 2 min. progressively; Curves 1, 3, 5 and 7 refer to 200 mM and Curves 2, 4, 6 and 8 to 400 mM of the salt.

Concn. of Murexide = 0·25 mM.
Concn. of HCl = 20 mM.
Temperature = 30° C.

murexide at $\lambda = 530\ m\mu$, at different concentrations of KCl, KBr, KI and KNO_3 present in the reaction mixture. It is instructive to note from the data in Figs. 5 and 6 that the value of the velocity constant k is the same for different salts as evidenced by the observation that the points representing $\log (r' - r)$ for KCl, KBr, KI and KNO_3 fall on the same line, $\log (r' - r)$ *vs.* t. It is therefore concluded that unlike in the case of inversion of sucrose, the

FIG. 5. Effect of the concentration of KCl on variation of log $(r' - r)$ with time.
Concn. of murexide = 0·25 mM.
Concn. of HCl = 20 mM.
Temperature = 30° C.
• 200 mM and ○-400 mM of KCl.

FIG. 6. Effect of different neutral salts on the variation of log $(r' - r)$ with time t.
Concn. of murexide = 0·25 mM.
Concn. of HCl = 20 mM.
Temperature = 30° C.
• KCl; ○ KBr; -○- KI and -⊙-; KNO_3.

anions of the acids or the added neutral salts have no significant effect on the velocity constant k of the decomposition of murexide. This observation is of marked importance and gives information about the nature, especially the electrically uncharged character, of the *reacting complex* undergoing change leading to the formation of the decomposition products of murexide, *viz.*, uramil and alloxan.

SUMMARY

The decomposition of murexide in acidic solutions was studied spectrophotometrically employing different strong acids like HCl, HBr and HNO_3 and mixtures of these acids and neutral salts like KCl, KBr, KI and KNO_3. The velocity constant k appeared to be a linear function of the concentration C of the strong acid used, and obeyed a relationship:

$$k/\text{min.}^{-1} = 2 \cdot 56 \times 10^{-3}\, C$$

The slope of the line was unaffected by the change in the nature of the acid or added salt indicating that the anions had no effect on the velocity constant.

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CONTENTS

PAGE

Nuclear Oxidation in Flavones and Related Compounds. Part L. A Synthesis of Ravenelin . . . . . V. K. Ahluwalia and T. R. Seshadri 1

Harmonic Analysis of the Spatial Flow of an Incompressible Viscous Fluid . . . . . S. K. Lakshmana Rao 6

The Role of Solvents in Chemical Reactions. Part III. The Reaction between Aniline and Methyl Iodide in Mixture of Solvents . . . . . V. S. Padmanabhan 13

Comparative Studies of Alternating and Direct Current Polarography: Effect of Concentration . . . . . N. A. Ramaiah and S. K. D. Agarwal 26

Synthetical Experiments in the Chromone Group. Part XXXII. A Synthesis of Tectorigenin . S. A. Kagal, S. S. Karmarkar and K. Venkataraman 36

Chemical Investigation of Indian Lichens. Part XX. A New Synthesis of Teloschistin . S. Neelakantan, T. R. Seshadri and Sankara Subramanian 42

Studies on the Kinetics of the Salt Effects on the Decomposition of Murexide in Acid Solutions . . . . N. A. Ramaiah, S. L. Gupta and Vishnu 46